The rate of charging of supercapacitors depends on how quickly ions can reach and accommodate the surface of electrodes. Diffusivity, a parameter reflecting the speed of ions' migration, is believed to be crucial in designing supercapacitor electrodes. Herein, this belief is questioned, shedding light on a puzzling and potentially critical feature of ionic dynamics denoted as confinement-induced ion–solvent separation. This effect can lead to a strong slowdown of the ion mobility inside hierarchical pore networks. Explanations for when such an effect occurs and how it can be circumvented are provided. Furthermore, this microscopic picture of diffusion seen by NMR is bridged with the macroscopic charging behavior of supercapacitors investigated by impedance spectroscopy. Quantifying the average residence time of ions within carbon particles shows that the nanopore environment may not be the rate-limiting factor for the overall ion mobility and thus performance of a cell—as commonly expected. Combining direct diffusion studies performed with neat and solvated ionic liquids and those on organic electrolytes, the so far lacking criteria for the rational selection of electrolyte–carbon systems is developed and recommendations for the preparation of transport-optimized materials for supercapacitors to minimize ionic diffusion limitations are given.

1. Introduction

An electrical double layer capacitor, also referred to as supercapacitor, is an energy storage device captivating through high power densities.[1] This advantage over classical battery systems is ensured by a purely physical storage mechanism of electrosorbed ions on the charged pore wall of porous carbon materials.[2] The rate-determining step, and thus the charge/discharge depends on the mobility of electrolyte ions within the supercapacitor cell, that is, by their diffusion, in particular also inside the pore system of the carbon electrode.[3] Complementarily to the conventional electrochemical characterization, multiple NMR approaches are increasingly applied to understand the electrolyte state and its dynamics within the carbon particles,[4,5] the carbon–electrolyte interactions,[6] and even to address exchange processes at the pore entrances.[7,8] An appeal of NMR techniques is in its operation on the micro-millisecond time scales, being hardly accessible in conventional electrochemistry. It allows observation of ionic dynamics on a microscopic level, that is, within the pore network of carbon particles, which is believed to determine the power capability of supercapacitors.

Seen in heterogeneous catalysis over zeolites,[9] it was suggested that the introduction of mesopores into the network of micropores assembling a hierarchical pore system promotes the ionic motion in carbon materials in a similar way.[10] Very recently, however, the direct diffusion measurements by means of pulsed field gradient (PFG) NMR unexpectedly revealed an opposite observation—the diffusion of the commonly used electrolyte (1 M tetraethylammonium tetrafluoroborate in acetonitrile, TEA-BF4/ACN) in a hierarchical model carbon was...
slowed down to the rates of diffusion in purely microporous materials, or even lower.[11] The hypothesis proposed to explain this counter-intuitive observation is that the electrolyte can undergo an ion–solvent separation at the interface of micro- and mesopores. In case of the investigated TEA-BF₄/ACN electrolyte, it has been speculated that adsorption of the ions is favored in the micropores, while the solvent tends to reside in the mesopores. However, both the experimental confirmation and the detailed understanding of this possible diffusion mechanism are lacking. It has been even more puzzling, scrutinizing why the electrochemical data obtained on the same carbon–electrolyte system did not exhibit signatures of an ultra-slow ionic dynamics in the hierarchical carbon (see Figure 2 in ref. [11]). This phenomenon, if confirmed, might lead to heavy implications upon development of high-performance hierarchical materials for supercapacitor electrodes. Therefore, we believe two tasks are crucial to be tackled now.

First, to survey and generalize the hypothesis of ion–solvent separation to avoid inaccurate implementation of the hierarchy principle in the design of the porous electrode materials. Assuming the separation is induced by the desolvation of ions, it should depend on the electrolyte concentration and it does not exist in the absence of a solvent. Expecting this, an ionic liquid-based electrolyte 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF₄) was selected for this study, which stays mobile at room temperature in its non-dissolved state. Its further dissolution in acetonitrile was applied to investigate an extent of confinement-induced “ion–solvent separation” and its impact on intra-particle diffusion within the hierarchical carbons.

Second, to elucidate the reason for the mismatch of the ion mobility at the microscopic level as determined by PFG NMR and the macroscopic level as observed by electrochemical characterization. Therefore, we quantified the characteristic times of confined diffusion inside pores of carbon (microscale) and the duration of (dis)charging (macroscale). The gained understanding clarifies a long-standing concern that the slow ionic dynamics inside pores of carbons may lead to diffusion limitations hampering the rate of (dis)charging of supercapacitor cells. Throughout the article, the terms diffusion and diffusivity in the NMR part refer to the self-diffusion and the self-diffusion coefficient, respectively, that is, in the absence of a gradient of electrical- and chemical potentials, while in the impedance spectroscopy, they include an ionic drift caused by applied electrical field.

2. Results and Discussions

2.1. Porous Model Carbons

As host materials, three model carbons with uniform and well-defined pores sizes were selected (Figure 1). These are: i) a microporous carbon (C_{micro}, a.k.a. TiC-CDC, 0.9 nm pore), ii) a mesoporous carbon (C_{meso}, a.k.a. CMK-3, 4.8 nm pore) and iii) a hierarchical carbon (C_{hierarch}, a.k.a. OM-CDC, 0.9 nm + 4.8 nm pore).[12–14] They were loaded with room temperature ionic liquid (RTIL) EMIM-BF₄ ions possessing dimensions of 0.76 × 0.43 nm (EMIM) and 0.48 nm (BF₄), in their desolvated state, and 1.4 and 1.16 nm with an acetonitrile (ACN) solvation shell, respectively.[15] Thus, only mesopores can host ions in their solvated state, while the desolvated ions can enter both micro- and mesopores.

2.2. Electrochemical Characterization of Model Carbons

Since ion mobility impacts the specific capacitance and the power of a supercapacitor, the materials have been electrochemically characterized for two different electrolytes, EMIM-BF₄ diluted in acetonitrile (1 m) and neat EMIM-BF₄ (6.6 m). It is important to note, no conducting agent (e.g., carbon black) was added during electrode manufacturing in order to not confound ion mobility properties. This however, leads to lower capacitances and higher resistances as commonly reported for such porous carbons. The ionic conductivity of the pure electrolytes; 1 and 6.6 m EMIM-BF₄ are determined with 60.8 and 18.30 mS cm⁻¹, respectively from electrochemical impedance spectroscopy (EIS). The higher conductivity of the diluted electrolyte is also observed in the Nyquist plot, as the impedance for all three materials is shifted to lower Re(Z) (Figure 2a). The capacitances, capacitance losses, and relaxation times of the three model carbons are displayed in Table 1. In both electrolytes, C_{hierarch} shows the highest and C_{micro} the lowest specific capacitance. Hence, the latter shows also the strongest capacitance decrease with increasing scan rate (Figure 2b) due to a slower diffusion and the large molecular radius of the ions. However, the retention of capacitance is improved by diluting the 6.6 m electrolyte,[16,17] Those carbons with mesoporosity (C_{meso} and C_{hierarch}) retain their capacitance also with faster charging and discharging rates. The
dilution of the 6.6 m EMIM-BF$_4$ is not significantly changing the rate handling performance. The relaxation time $\tau_0$ (time related to the discharging of the cell\cite{18}) strongly decreases for all model carbons, if the electrolyte is diluted (Figure 2c,d). This can be quantified by the ratio of $\tau_{0(6.6\text{M})}/\tau_{0(1\text{M})}$ (Table 1). This ratio is larger for C$_\text{micro}$ than for C$_\text{meso}$, which means that electrolyte dilution is mainly affecting the diffusion in the micropores and less the diffusion in the mesopores—an observation which will become important later on. Likewise, the real part of the capacitance $C'$ (Figure 2e,f) does not run into a plateau at low frequencies for those carbons with micropores (C$_\text{hierarch}$ and C$_\text{micro}$) if the 6.6 m electrolyte is used.\cite{29} If the full capacitance (plateau) cannot be reached even at low frequencies of voltage alternation, ions exhibit severe diffusion limitations. Diluting the electrolyte leads to an improved plateau formation for all three carbons.

### 2.3. Diffusion of Ions by Pulsed Field Gradient NMR

The self-diffusion coefficients of ions measured in carbons by PFG NMR are summarized in Table 2. The full set of diffusion data including attenuation curves, aspects of their processing and detailed discussion of obtained values in the

| Carbon  | Electrolyte | $C_{\text{Spec}}$ [F g$^{-1}$] | $C_{\text{loss}}$ [%] | $t_2$ [s] | $t_{0(6.6\text{M})}/t_{0(1\text{M})}$ |
|---------|-------------|-------------------------------|----------------------|----------|----------------------------------|
| C$_\text{micro}$ | 6.6 m | 33 | 35 | 61 | 5.5 |
| C$_\text{micro}$ | 1 m | 28 | 19 | 11 | |
| C$_\text{meso}$ | 6.6 m | 45 | 10 | 6 | 3.0 |
| C$_\text{meso}$ | 1 m | 44 | 9 | 2 | |
| C$_\text{hierarch}$ | 6.6 m | 74 | 6 | 20 | 4.0 |
| C$_\text{hierarch}$ | 1 m | 68 | 7 | 5 | |

Figure 2. The electrochemical characterization of the model carbons C$_\text{micro}$ (triangle, grey), C$_\text{meso}$ (circle, blue), and C$_\text{hierarch}$ (square, red) measured in the two different electrolytes. Painted symbols represent the 6.6 m EMIM-BF$_4$, empty symbols represent the 1 m EMIM-BF$_4$. a) Nyquist plot; b) specific capacitance calculated with different specific charge-discharge currents; c,d) imaginary part of the capacitance $C''$ at different frequencies; e,f) real part of the capacitance $C'$ at different frequencies.
ties from approximately threefold in micro to \( \approx 10^2 \) \( \text{C} \) for EMIM- and BF\(_4\)-ions in bulk solutions and confined to \( \text{C}_{\text{micro}} \), \( \text{C}_{\text{meso}} \), and \( \text{C}_{\text{hierarch}} \) for EMIM-BF\(_4\) and EMIM-BF\(_4\)/d-ACN at room temperature. \( D_1 \) and \( D_2 \) represent the self-diffusion coefficient measured in the directions parallel and perpendicular to the bundles orientation, respectively. The suffix “expected” describes the theoretically-expected diffusivity of a material as a sum of its weighted micro- and mesopore diffusivities.

Diffusion resistances of 6.6 m—(pyramids, first row to the reader) and ACN-solvated 1 m EMIM-BF\(_4\) (boxes, second row) electrolytes in various systems. For comparison, data obtained on 1 m TEA-BF\(_4\)/ACN in ref. [11] are represented. The DUTY-factors obtained for anions are always higher than those of cations suggesting that dilution of EMIM-BF\(_4\) by ACN increases the anionic mobility more efficiently. This is probably due to more isotropic shape of a BF\(_4\)-ion, which can easier form a solvation shell around itself promoting the ionic diffusion, compared to the elongated shape of EMIM-cation.

When electrolyte is adsorbed inside carbon, both factors dilution and type of confinement will affect diffusivity of the ions. In order to bare an impact of confinement, it is convenient to convert absolute values of the self-diffusion coefficients into diffusion resistances, that is, normalizing as \( D_{\text{bulk}}/D_{\text{pore}} \). Such representation, illustrated in Figure 3, demonstrates the degree of suppression of ionic diffusion inside pores of materials in comparison to unrestricted bulk diffusion of the same electrolyte and will be further followed unless otherwise stated.

For neat EMIM-BF\(_4\) (6.6 m) the confinement-induced diffusion resistances were found to be relatively low (pyramids in context of electrolytes structure and pores confinement is provided in the method section and in Supporting Information. Depending on the type of electrolyte and confinement the absolute values of diffusivities span over four orders of magnitude, being expectedly rapid in the diluted bulk electrolyte (e.g., \( 1.74 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) for anion) and least mobile when measured with a neat IL diffusing in micropores (e.g., \( 4 \times 10^{-12} \text{ m}^2 \text{s}^{-1} \) in \( \text{C}_{\text{micro}} \)) or perpendicular to the orientation of mesopores (e.g., \( \approx 2 \times 10^{-11} \text{ m}^2 \text{s}^{-1} \) in \( \text{C}_{\text{hierarch}} \)). It is worth noting that in \( \text{C}_{\text{meso}} \) and \( \text{C}_{\text{hierarch}} \) the data revealed pronounced anisotropic diffusion consistent with their 1D mesopore channel architecture (Figure 1). This allowed the measurement of ionic diffusivities in the directions parallel (\( D_1 \)) and perpendicular (\( D_2 \)) to the orientation of primary carbon nanorods. If not stated explicitly, \( D_1 \) is used in all further considerations. When diffusivities are compared between different carbons the following common trend is observed \( \text{C}_{\text{micro}} < \text{C}_{\text{hierarch}} < \text{C}_{\text{meso}} \) (Figure 3). The dilution of a neat electrolyte with the solvent ACN always resulted in higher diffusivities from approximately threefold in \( \text{C}_{\text{micro}} \) to \( \approx 39\)-fold in the bulk solutions. This enhancement, introduced as the ratio of respective diffusivities \( D_{\text{M}}/D_{\text{6.6M}} \) and called a “DUTY-factor”, revealed differences when the cations and anions and compared with each other. The DUTY-factors obtained for anions are always higher than those of cations suggesting that dilution of EMIM-BF\(_4\) by ACN increases the anionic mobility more efficiently. This is probably due to more isotropic shape of a BF\(_4\)-ion, which can easier form a solvation shell around itself promoting the ionic diffusion, compared to the elongated shape of EMIM-cation.

Figure 3. The diffusion resistances of 6.6 m (pyramids, first row to the reader) and ACN-solvated 1 m EMIM-BF\(_4\) (boxes, second row) electrolytes in various systems. Green tags represent the self-diffusion coefficient measured in the directions parallel and perpendicular to the bundles orientation, respectively. The suffix “expected” describes the theoretically-expected diffusivity of a material as a sum of its weighted micro- and mesopore diffusivities.
the first row). It is prominently seen for cations in \( C_{\text{meso}} \) being only 1.7 times slower as in the bulk electrolyte. A maximum value of 11 is obtained for anions inside \( C_{\text{micro}} \). This relatively low impact originates from the initially strong contribution of Coulomb interaction between counter-ions present in an IL electrolyte. It results in already low ionic diffusivity in the bulk neat IL (\( D_{\text{bulk}} \approx 10^{-12} \text{ m}^2 \text{ s}^{-1} \)) as compared to neutral liquids with comparable molecular size or solvated electrolytes. Usually, it is expected that the presence of micropores reduces diffusivity by several orders of magnitude (see, e.g., Figure 2a of ref. [4]). However, in the case of a neat IL, the nanoconfinement (even the micropores) only moderately affects the ionic dynamics with respect to the bulk.

When the same electrolyte is diluted with ACN, its bulk ionic diffusivities increase up to \( D_{\text{bulk}} = 10^{-9} \text{ m}^2 \text{ s}^{-1} \). Now, the role of pore confinement becomes increasingly significant—the diffusion resistances increase to \( \approx 100 \) in \( C_{\text{micro}} \), \( \approx 10 \) in \( C_{\text{meso}} \), and \( \approx 15 \) \( C_{\text{hierarch}} \) (boxes in the second row). Along with it, the dilution decreases the diffusion resistance only by factors \( \approx 3 \) in \( C_{\text{micro}} \), \( \approx 7 \) in \( C_{\text{meso}} \), and \( \approx 10 \) \( C_{\text{hierarch}} \) (see DUTY-factors), while in the bulk the DUTY-factor is much higher, that is, \( \approx 35 \). Although dilution can efficiently speed up ions in the bulk phase due to substantial screening of Coulombic forces between them, it does not appear to a similar extent inside carbons. In the latter case, different types of pores lead to different constraints, but also to different degrees of ionic solvation (e.g., a micropore is too narrow to accommodate an ion with a full solvation shell), which altogether affects the ionic mobility compared to bulk unrestricted diffusion of fully solvated ions.

The above diffusion trends, \( C_{\text{micro}} < C_{\text{hierarch}} < C_{\text{meso}} \), are also captured by molecular dynamics simulations (see simulated values in Table S3, Supporting Information). This is despite using highly idealized structural models, which suggests diffusivity is predominantly dictated by the differences in pore sizes of the carbon materials. The obtained values of diffusivity are qualitatively produced, however, the simulated DUTY factors are not. It is difficult to reproduce precise trends by simulations owing to the idealized models employed, which feature 2D channels and the limited sampling possible by atomistic simulation approaches. However, the simulations are able to highlight differences in local structure of the ions.

Analysis of the radial distribution function (RDF) for the carbon ring atom and boron atom of the EMIM-BF₄ solutions demonstrates the probability of finding atom distances for the obtained trajectories. As expected, the dilution of the ions, from 6.6 to 1 m, in the \( C_{\text{hierarch}} \) and \( C_{\text{meso}} \) structures, which feature large mesopore channels, lead to a decrease in the probability of pair distances greater than 8 Å implying the formation of large clusters of ions is suppressed (Figure 4). For \( C_{\text{micro}} \) structure, however, it is observed that these large clusters with cation and anion pairs are lacking and only first and second neighbors, at \( r = 4 \) and \( r = 6 \) Å, are present. This suggests that the micropore confinement restricts the formation of larger clusters. Moreover, the dilution of the electrolyte within the micropore is shown to affect the packing of the ions significantly as the peaks attributed to the first and second neighbors are affected. Simulation of these ion structures support the experimental observations as diffusion can be significantly increased by the disruption of larger clusters by dilution. This will have a smaller affect in micropore environments where these larger clusters cannot form.

For 1 and 6.6 m EMIM-BF₄ electrolytes, the diffusion resistance in \( C_{\text{hierarch}} \) are lower than in \( C_{\text{micro}} \) and higher than in \( C_{\text{meso}} \). This is intuitively expected as the material depicts a carbon consisting of 26 vol% micropores and 74 vol% mesopores. The most striking observation here, however, is the opposite diffusion behavior of 1 m EMIM-BF₄/ACN compared to the diffusion of 1 m TEA-BF₄/ACN organic electrolyte in the same material as it was reported in our previous study.[11] In \( C_{\text{hierarch}} \), the diffusion resistances seen for both neat and solvated IL (presented by pyramids and boxes in Figure 3) are dramatically lower than those measured with organic electrolyte (shown as cylinders in a third row for comparison). The obtained diffusivities \( D_{\text{hierarch}} \) and respective diffusion resistances matched well those derived using the model proposed for calculation of expected diffusivity in \( C_{\text{hierarch}} \). The model is based on measured diffusivity inside micropores \( (D_{\text{micro}}) \) and mesopores \( (D_{\text{meso}}) \) weighted according to their relative pore volumes (details are described in Supporting Information). The respective values are denoted as “expected” and presented for each electrolyte in Table 2 as \( D_{\text{hierarch(expected)}} \) and in Figure 3 under \( C_{\text{hierarch(expected)}} \). Remarkably, while in case of organic electrolyte measured diffusion resistances were orders of magnitude higher than the expected ones (1379 versus 17 for cations), in the solvated IL they appeared to be very close (13.0 versus 12.4). The same trend is seen also for anions. This observation confirms the hypothesis of a local ion-solvent separation occurring upon entering the micropores from the mesopore that has been proposed for a case of ACN-solvated TEA-BF₄ electrolyte in a hierarchical carbon \( C_{\text{hierarch}} \).[11] As this takes place, the local ion concentration within the micropore and thus the ion-ion attraction will become as higher, as stronger is the separation.

![Figure 4](image-url). Radial distribution functions \( g(r) \) between the CR atom of EMIM and the B atom of BF₄ (pictured) at 6.6 m and diluted 1 m concentrations in ACN simulated within the pore models over a 10 ns trajectory at 300 K.
This leads to a significant suppression of ionic mobility inside micropores observed for confined ACN-solvated TEA-BF₄ electrolyte. This however, is not expected to take place in an IL electrolyte which remains mobile due to the inability to form a crystallite at room temperature, even when it is fully separated from its solvent molecules. The observed separation phenomena may occur due to a number of solvation mechanisms surveyed in, for example, ref. [19] originating from the specific intermolecular and molecule–pore wall interactions.

This hypothesis of local ion–solvent separation was investigated by careful analysis of the trajectories produced by the molecular dynamics study. The density distribution of EMIM/BF₄ ions and ACN-solvent within pore structures representative of the C micro, C hierarch, and C meso pore environments were computed, in addition to a C hierarch system containing TEA/BF₄ at 1 m dilution with ACN (Figures S10–S12, Supporting Information). The simulated distributions demonstrate the preferred double layer structure that EMIM and BF₄ produce when confined in the micropore and the multilayer formation and clustering possible in the larger mesopores in agreement with the RDF analysis. These distributions show large changes when diluted with ACN. First, dilution produces more homogeneous distribution of ions in the mesopores with the high density clustering no longer observed. Second, in the micropore, the disparate layer structures of the ions and the solvent disrupt ion–ion attraction leading to a lack of the double layer ordering noted for BF₄ ions in the C micro and C hierarch pore environments. This is a consequence of the stark difference in carbon–ion distances of EMIM and BF₄ in the 1 m systems. The density of BF₄ in each of the pore systems is found to extend further from the carbon surface, whereas there is no difference perceived for the 6 m system. This can also be ascertained from RDF analysis of the carbon, CR, and B atom distance pairs (Figure 4). Similar interactions and resulting distances of BF₄ to the carbon pore walls were also reported previously by NMR techniques.[100] The planar structure of the EMIM core is susceptible to the carbon pore walls were also reported previously by NMR techniques.[100] The planar structure of the EMIM core is susceptible to the carbon pore walls were also reported previously by NMR techniques.[100] The planar structure of the EMIM core is susceptible to carbon–ion interactions and the outcome for this density distribution for TEA is the aim of ongoing molecular dynamics computation studies.

According to the obtained data, it turns out that an extent of separation influencing diffusivity is as larger, as higher is the measured diffusion resistance compared to the expected one. In contrast, their proximity would mean small or no effect of ion–solvent separation on ionic diffusion. In order to estimate impact of this effect on electrolyte diffusion inside a hierarchical carbon of interest, we propose a simple "5-steps-check" (Figure 5) consisting of five actions: 1—measurement of diffusivity in the hierarchical carbon consisting of smaller (e.g., micro-) and larger (e.g., meso-) pores, 2 and 3—measurement of diffusivities in the carbons maximally mimicking porosity of smaller and larger pores of the hierarchical one, 4—calculation of expected diffusivity (or diffusion resistance) for the hierarchical carbon using the proposed model, and 5—comparison of the diffusivity measured in step 1 with the expected one derived in the step 4. Check the result: if \( D_{hierarch} \approx D_{hierarch(expected)} \), there is negligibly small or no negative impact of an ion–solvent separation on the ionic diffusion in the hierarchical carbon. Alternatively, if \( D_{hierarch} < D_{hierarch(expected)} \) (or measured diffusion resistance > than the expected one), there is slowdown of ionic dynamics caused by a separation and thus effectively higher ionic concentration in smaller pores. In the latter case, the larger is the deviation, the stronger is the effect.

### 2.4. How Significant is the Impact of In-Pore Dynamics upon Charging of a Supercapacitor?

The observations of the previous section illustrate that similar type of confinement can lead to different implications on the ionic diffusion in porous materials. The central question that arises from that is: How significant are these microscopic processes when considered in the context of a macroscopic ion mobility and thus the power characteristics of a supercapacitor? To address this question, we suggest linking the results of PFG NMR with EIS in a complementary way. By doing so, the ionic dynamics can be tackled at micro- and macro-scales by estimating the characteristic times of the processes involved in the cell’s (dis)charging. To facilitate this approach, three primarily contributing processes can be mentioned, namely: a) diffusion outside pores of carbon, b) confined diffusion...
inside pores and (c) possible rearrangement of ions within pores to form a double layer at the electrolyte–carbon interface. The nature of the latter process, also referred to as phase transition,

have been discussed in details for ionic liquids in the works of Oschatz et al. These processes are illustrated in Figure 6 along with a characteristic time scales \( t_{\text{NMR}} \) and \( \tau_0 \) that can be deduced from the PFG NMR and EIS, respectively. The parameter \( t_{\text{NMR}} \) represents the time needed for an ion to travel through a carbon particle of a given size and can be obtained from the measured in-pore diffusivities of the previous chapter (see Supporting Information for details). The relaxation time constant \( \tau_0 \) introduced by Taberna et al. and representing the total (dis)charging time of a cell is obtained from the Nyquist plots in Figure 2(c,d) and provided in Table 1. The obtained characteristic times for studied electrolyte–carbon systems are summarized in Table 3. It is worth adding that the time required to transfer the charge through the studied carbons is negligible as their intrinsic electric conductivity is orders of magnitude higher than the ions’ conductivity.

From the data presented in Table 3, several conclusions can be made. The time needed to displace ions within carbon particles \( t_{\text{NMR}} \) is always shorter than the time of discharging \( \tau_0 \). This suggests that the majority of ions at least once leave or enter the nanopore space of carbon particles upon the supercapacitor charging. This supports an observation made by Forse et al. using in situ characterization studies. They stated that supercapacitor charging can either be facilitated by ions' in-pore diffusivities. An opposite extremum of \( t_{\text{NMR}}/\tau_0 \) would correspond to the case of a severe diffusion limitation, that is, when ions during charging rarely or do not leave their original intra-particle space, and the entire process is controlled by ions' in-pore diffusivities. An opposite extremum of \( t_{\text{NMR}}/\tau_0 = 0 \) would reflect an infinitely high rate of diffusion compared to the rate of (dis)charging. The obtained \( t_{\text{NMR}}/\tau_0 \) ratios vary from 0.01 to 0.15 suggesting low impact of in-pore ionic diffusion for used electrolyte–carbon systems. It is important to mention that the estimation of \( t_{\text{NMR}} \)-values does not account for possible readsorption events, that is, when an ion explores more than one carbon particle, which will increase its total residence time inside pores. The rate molecular readsorption process being proportional to a sticking probability is a long-standing problem not only in energy storage processes, but also in, for example, heterogeneous catalysis or separation. Its experimental detection is challenging and requires special consideration.

The maximum \( t_{\text{NMR}}/\tau_0 \) value of 0.15 obtained for 1 m TEA-BF4/ACN in \( C_{\text{micro}} \) demonstrates that the ionic in-pore diffusion is by far not a rate-limiting step in the (dis)charging process, even when the microporous carbon with the pore sizes being comparable to the bare cationic diameter is used. Instead, the processes of diffusion through the bulk electrolyte medium outside the particles and/or the process of the ionic rearrangement upon formation of the double layer on the carbon surface limit the power characteristics of studied electrolyte–carbon systems. This, at the first glance counterintuitive statement, can be rationalized, if we recall that \( t_{\text{NMR}} \) is proportional to the square of the carbon particle size, while the dependence on diffusivity is \( \sim D^{-1} \) and thus, weaker. For 1 m TEA-BF4/ACN in \( C_{\text{hierarch}} \), for which unexpectedly ultra-slow ionic diffusion was reported, \( t_{\text{NMR}}/\tau_0 = 0.12 \) was obtained. Even in such case, the need to cover the distance to exit the carbon particle (i.e., the shortest pathway to exit \( C_{\text{hierarch}} \) being perpendicular to the carbon bundles and reaching up to 1 \( \mu \)m) with measured diffusivities still results in notably shorter time \( t_{\text{NMR}} \) compared to \( \tau_0 \) (5.2 s). It is worth mentioning that the situation will change dramatically, if larger particles are used. The experimentally obtained values of \( t_{\text{NMR}} \) for used carbons with their corresponding actual particle sizes

Table 3. Estimated times for cell (dis)charging \( \tau_0 \), the residence time of ions inside carbon particle \( (t_{\text{NMR}}) \) and their ratio \( t_{\text{NMR}}/\tau_0 \) for all studied electrolyte solutions and carbons.

| Electrolyte solution | \( C_{\text{micro}} \) | \( C_{\text{macro}} \) | \( C_{\text{hierarch}} \) |
|----------------------|----------------------|----------------------|----------------------|
|                      | \( \tau_0 \) [s]     | \( t_{\text{NMR}} \) [s] | \( t_{\text{NMR}}/\tau_0 \) | \( C_{\text{micro}} \) | \( C_{\text{macro}} \) | \( C_{\text{hierarch}} \) |
| 1 m TEA-BF4/ACN      | 10.4                 | 1.6                  | 0.15                 | 2.9                  | 0.1                  | 0.03                 | 5.2                  | 0.6                  | 0.12                 |
| 1 m EMIM-BF4/ACN     | 10.8                 | 0.2                  | 0.02                 | 2.2                  | 0.1                  | 0.05                 | 5.0                  | 0.1                  | 0.02                 |
| 6.6 m EMIM-BF4       | 60.8                 | 0.7                  | 0.01                 | 5.9                  | 0.3                  | 0.05                 | 20.0                 | 2.5                  | 0.13                 |

For obtained \( t_{\text{NMR}} \) values presented in the Table S2, Supporting Information, the larger one between the cation and anion is selected for presenting here.
sizes are provided in Table S2, Supporting Information. Simple estimate demonstrates that already twice thicker particles (bundles) of $C_{\text{hierarch}} (=2 \mu m)$ will result in fourfold higher $T_{\text{NMR}}$, that is, 2.3 s, and potentially lead to appearance of diffusion limitations originating from the in-pore diffusion.

Based on the presented study, a few aspects that may help to rationally prepare materials for supercapacitors can be discussed.

1. The analysis of the obtained residence times for ions within the carbon particles revealed that the average particle size is one of the characteristics crucially influencing the power characteristics of a supercapacitor. In fact, the aspects of intra-particle ionic diffusion may not necessarily be even taken into account, when the particles are small enough. Based on existing data, we estimate this cut-off size as few $\mu m$. In contrast, when individual particles are larger than few tens of $\mu m$, the entire charging process will probably be controlled by the ionic diffusion inside pores of carbon. Obviously, the exact limits for critical particle sizes will be system-specific.

2. Depending on the type of electrolyte, ion diffusivity can change by orders of magnitude. In the absence of carbons, neat ionic liquids exhibit notably lower diffusivities compared to their diluted counterparts. However, when former confined to micropores change in the ionic mobility might be within an order of magnitude maximum. A prominent example of it is tenfold lower diffusivity of a neat EMIM-BF$_4$ inside microporous carbon, which pore size ($=0.9$ nm) is comparable to the bare cation size ($=0.8$ nm), compared to unrestricted bulk diffusion. Presence of mesopores reduces this difference only down to $\approx2$, also revealing similar result for a hierarchical carbon---2 and $\approx3$ for EMIM- and BF$_4$ ions, respectively. Thus, as long as pores are accessible, the pore size of carbons does not play a critical role for ionic diffusion when neat ionic liquids are used.

3. In contrast to this, for diluted electrolytes in which bulk ionic mobility approach values of a solvent, the presence of micropores reduces the diffusivity by two to three orders of magnitude, and pore hierarchically seems to be highly recommended. Indeed, in the case of diluted IL (1 m EMIM-BF$_4$/ACN), the effective diffusivity in the hierarchical carbon closely approaches that of a mesoporous one. Therefore, the hierarchical carbons are highly recommended for IL-based electrolytes (neat and solvated).

However, when organic electrolytes are used requiring a solvent to stay mobile, the presence of a pore hierarchy may result in an opposite effect—ultra-slow ionic diffusion due to possible ion-solvent separation, that is, becoming even slower than in purely microporous carbon. Thus, special attention is required in the case of organic-based electrolytes when used with hierarchical carbons.

3. Summary and Conclusion

The present contribution provides an understanding of the ionic dynamics on the microscopic and macroscopic levels in model carbons including those possessing pore hierarchy. We demonstrate that the utilization of a room temperate ionic liquid EMIM-BF$_4$ (neat and diluted with acetonitrile) as electrolyte eliminates problem associated with the effect of “ion–solvent separation” leading to ultra-slow ionic diffusion in hierarchical carbons observed previously for organic electrolyte (1 m TEA-BF$_3$/ACN). By using the proposed “5-steps-check,” the impact of such effect on the in-pore ion diffusion can be identified. Remarkably, even when the latter takes place, it may still be not a rate-limiting process in the charging–discharging cycles of a supercapacitor. The size of an individual carbon particle seems to play a decisive role. To address this quantitatively, a complementary approach by combination of PFG NMR and electrochemical techniques allowed to access average residence time of ions inside carbon particles and compare it with characteristic time of a cell discharge. It is demonstrated that using a standard technique of a cell preparation, for particles smaller than few micrometers in size, ionic diffusion inside pores is not a rate-limiting factor in the process of cell (dis)charging. Instead, other mechanisms may dominate, that is, diffusion in the inter-particle space and/or ions' rearrangement upon formation of a double layer. Based on this observation, we believe that for the preparation of carbons for a high-power supercapacitor applications, the particle size should be considered on a first place and ideally analyzed in the context of residence times of ions inside carbon particles derived from direct diffusion studies. Additionally, several recommendations toward rational preparation of materials for supercapacitors are provided.

4. Experimental Section

**Synthesis of $C_{\text{meso}}$:** The titanium carbide derived carbon was prepared by high temperature chlorine treatment of crystalline TiC powder (Sigma-Aldrich, 95%, 325 mesh). For the chlorination step, 1.0 g of the TiC powder was transferred into a tubular quartz furnace. After 30 min of flushing the sample with 150 mL min$^{-1}$ Ar, the material was heated to 1000 K with a rate of 450 K h$^{-1}$. The gas composition was changed to 80 mL Ar min$^{-1}$ and 70 mL Cl$_2$ min$^{-1}$. After 3 h of chlorination, the furnace was switched off and cooled down to 873 K under an Ar flow of 150 mL min$^{-1}$. The gas flow was changed to 80 mL H$_2$ min$^{-1}$ for 1 h to remove adsorbed chlorine from the pores.

**Synthesis of $C_{\text{micro}}$:** 2.0 g of hexagonally ordered mesoporous SiO$_2$ template (SBA-15) was dispersed in 10 mL aqueous solution of 2.5 g sucrose and 0.28 g 96% sulfuric acid. The mixture was heated at 373 K for 3 h and as 433 K for another 3 h. The same infiltration procedure was repeated with the resulting composite and a 10 mL aqueous solution of 1.6 g sucrose and 0.18 g 96% sulfuric acid. Carbonization was carried out under 150 mL min$^{-1}$ argon atmosphere in a horizontal tubular furnace at 1173 K with a heating ramp of 150 K h$^{-1}$ for 2 h. SiO$_2$ was removed by dispersing the composite in hydrofluoric acid (35% aqueous solution)-water–ethanol mixture (1:1 by volume) for 24 h followed by washing with large amounts of ethanol. Residual HF was deactivated by mixing the solution with saturated CaF$_2$ solution. The sample was dried at 353 K for 24 h under vacuum.

**Synthesis of $C_{\text{hierarch}}$:** Similar to $C_{\text{meso}}$, 2.0 g of hexagonally ordered mesoporous SiO$_2$ template were infiltrated with a mixture of 2.1 mL of poly(vinylidene) precursor SMP-10 and 0.5 mL of the cross linking p-divinylbenzene by the incipient wetness method. Carbonization was carried out under 150 mL L$^{-1}$ argon atmosphere in a horizontal tubular quartz furnace at 1073 K with a heating ramp of 60 K h$^{-1}$ for 2 h. The SiO$_2$ template was removed according to the synthesis of $C_{\text{meso}}$. Thereby, a hexagonally ordered mesoporous SiC (OM-SiC) was formed. OM-SiC was converted to the hierarchical porous $C_{\text{hierarch}}$ by chlorination at 1173 K similar to the synthesis of $C_{\text{meso}}$.

**Ionic Conductivity Measurement of Electrolytes:** The ionic conductivity of neat (6.6 m) and diluted (1 m) EMIM-BF$_4$ were measured with...
a Greisinger GMH 5450 combined with a LF425 conductivity probe (four poles) consisting of graphite.

**Electrochemical Characterization:** The carbon electrodes were fabricated as free-standing electrodes in a dry process out of the carbon powders. The powders were ground with 5 wt% PTFE as binder in an agate mortar at 80 °C until a dough-like mass was obtained. The mass was further rolled out at 80 °C until the electrode film had a thickness of 120 μm. The electrode films were dried in a vacuum oven at 80 °C for 24 h. With a disc cutter, electrodes with a diameter of 10 mm were cut. The characterization was done in custom-built cells in a symmetrical two-electrode setup with either 6.6 M EMIM-BF4 or 1 M EMIM-BF4 in acetonitrile as electrolyte. The electrodes were pressed on titanium steel current collectors, which were coated with a conductive carbon slurry (ElectroDAC purchased by Henkel) in advance. As separator, 12 mm diameter Whatmann GF/D were used. The cells were prepared inside a glovebox under inert gas atmosphere.

The electrochemical measurements were performed with a Biologic VMP-3 potentiostat/galvanostat. Cyclic voltamograms were conducted with different scan rates in the range from 5 mV s⁻¹ to 1 V s⁻¹. Galvanostatic charge-discharge curves were conducted with specific currents from 0.1 to 15 A g⁻¹. Between the charging and discharging an open circuit voltage was applied for 10 s. Impedance spectroscopy was recorded with an amplitude of 10 mV in a frequency range from 5 mHz up to 200 kHz. Transversal relaxation time \( \tau \) was calculated according to reference. [29]

**Sample Preparation for PFG NMR Experiments and Data Analysis:** All three carbon materials were loaded with a volume of electrolyte according to the pore volume obtained by N₂ physisorption. For \( \text{C}_{\text{meso}} \) and \( \text{C}_{\text{hierarch}} \) this leads to ~100% pore filling. For \( \text{C}_{\text{micro}} \), however, this cannot be assured since porosity properties screened by the adsorption of N₂ (kinetic diameter of 0.36 nm) do not necessarily match the “experienced” porosity of bigger EMIM and BF₄ ions (0.75 × 0.43 and 0.48 nm). Small ultramicropores might be either unfilled or only partially filled by EMIM-BF₄.

The capillaries for the PFG NMR measurements were prepared according to the following procedure described with 100% of the absolute pore volume, which was determined by nitrogen physisorption experiments in advance.

First, each carbon powder has been infiltrated by 6.6 M EMIM-BF₄ or 1 M EMIM-BF₄ in d-ACN to 50% pore volume via incipient wetness method inside a glove box under inert atmosphere. Deuterated solvent was used for the dilution of EMIM-BF₄ to eliminate the interference of the proton signal coming from ACN molecules with the proton signal from cations. Then carbons were transferred into NMR glass tubes, which had an outer diameter of 7.7 mm and neck at 80 mm height, such that the height of the material in the tube has reached 10 mm. The rest of the 50% pore volume was loaded to carbons directly in NMR tubes that the height of the material in the tube has reached 10 mm. The rest which had an outer diameter of 7.7 mm and neck at 80 mm height, such to 1 V s⁻¹ of N₂ (kinetic diameter of 0.36 nm) do not necessarily match the classical force field developed by Canongia Lopes et al. was used for EMIM and BF₄ ions, a three-site model was used for acetonitrile and OPLS-AA for the carbon surface, which was treated as fixed throughout the simulation. [31-32] The dispersion interactions were described using a Lennard–Jones potential and the cross-parameters were obtained from the Lorentz–Berthelot mixing rules of like-atom pairs. The electrostatic interactions were calculated using the particle–particle particle–mesh technique with an accuracy of 10⁻⁵ and the non-bonding interactions were cut-off at 12 Å. [36]

Initial configurations were produced with the packmol software [37] to pack either 6 M of EMIM-BF₄ into the structures or 1 M EMIM-BF₄ with a concentration of acetonitrile of ~16 M. Molecular dynamics trajectories were computed in the NVT ensemble using a timestep of 1 fs and the temperature was controlled using the Nosé–Hoover thermostat with a relaxation time parameter of 1000 fs. [38,39] For each system an initial 1 ns equilibrium run was performed at \( T = 1000 \) K followed by an equilibration period of 1 ns before acquiring data in a final production run of 10 ns. Mean-squared displacements, radial distribution functions and global distributions were computed from the production trajectories using the MDAnalysis Python library. [40] Diffusivities were computed from the slope of mean-squared displacement using the Einstein relation. [41]

Representative input files can be found on the Github repository of Jack D. Evans, https://github.com/jackevansad/supp-data.

**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.

Data Availability Statement
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