Temperature-independent capacitance of carbon-based supercapacitor from −100 to 60 °C

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ABSTRACT

Building supercapacitors that can provide high energy density over a wide range of temperatures, where traditional energy storage devices fail to operate, requires tailoring of electrolyte and/or electrode material. Here, we show that record gravimetric capacitances of 164 and 182 F g⁻¹ can be attained at −100 and 60 °C, respectively, nearly equal to the room-temperature value of 177 F g⁻¹, when activated carbon-based electrodes with predominantly slit-shaped micropores and a low freezing-point electrolyte are used. Experimental data and density functional theory calculations suggest that electrode material characteristics, such as pore size and shape, matched with the effective size of partially solvated ions of the electrolyte, are the key factors in achieving such performance. This study provides evidence for the effective design of robust supercapacitors with sustained performance at both low and high temperatures.

1. Introduction

Energy storage devices capable of storing/delivering energy for thousands of cycles at high charge/discharge rates in conditions where temperature can vary wildly, such as at high altitudes, are necessary for meeting the needs of aerospace and other industries [1,2]. Current lithium-ion and lead-acid batteries cannot operate under extreme temperature conditions [3,4]. Electrochemical double-layer capacitors (EDLCs) offer promise towards achieving reliable operation in a wide range of temperatures (i.e., from −70 to 80 °C) because their energy storage mechanism relies only on the electrostatic adsorption and desorption of electrolyte ions [5–7]. However, commercial EDLCs can only operate down to about −40 °C due to freezing points of their solvents, acetonitrile (ACN) or propylene carbonate being −45 and −25 °C, respectively [8,9] (Scheme 1). Extending this operating temperature down to −70 °C involves modification of the electrolyte (use of mixed solvent systems and/or different salts) aimed at decreasing its freezing temperature and minimizing conductivity decrease as temperature decreases [6,10]. For example, compared to a pure ACN-based EDLCs, a 1:1 mixture of ACN/1,3-dioxolane (DIOX) extended this operation temperature down to −70 °C. However, the capacitance dropped significantly compared to the room-temperature value [6]. Further, compared with tetraethylammonium tetrafluoroborate (TEA-BF₄), the specific capacitance of microporous carbon increased by four times at a scan rate of 100 mV s⁻¹ when spiro-[1,1]-bipyroridinium tetrafluoroborate was used in a 1:1 ACN/methyl formate mixture at −60 °C [10]. Porous carbons, including activated carbons (ACs), have been widely used as electrode materials in EDLCs due to their high specific surface area (SSA) [5,11–14]. However, it is presently not well understood how the pore size and morphology of ACs affects EDLC performance at
ultra-low temperatures.

In this work, we synthesized ACs with a bimodal distribution of micropores and mesopores, and with predominantly slit-shaped pores. This pore morphology, which is tunable in both size and shape, enables access of the high surface area of the ACs by the solvated ion clusters during EDLC operation in a wide temperature range of 100°C to 60°C (Scheme 1). This work experimentally demonstrates how the shape and size of the pores in ACs can be matched with the effective size of partially desolvated triethyl methyl ammonium (MeEt3N+) ions in an ACN/DIOX mixed solvent system to ultimately yield exceptional EDLC performance (164 F g⁻¹ and 92.6% capacitance retention at 5 mV s⁻¹) even at 100°C. We propose a temperature-dependent ion desolvation model, combined with DFT calculation of binding energy between ions and solvents, to validate the experiment results.

2. Results and discussions

2.1. Preparation and characterization of activated carbons

We prepared the soymeal-derived ACs by a carbonization-activation process (Fig. S1). These ACs were used in making the coin cell supercapacitors and are referred to as AC-X, where X stands for the KOH to carbonized coke ratio used during activation. This two-step AC preparation process can result in ACs with a range of physical properties depending upon the carbon source and processing. In our work, the XRD pattern of AC-0 shows a broad (002) peak at a 2θ of ~25° (Fig. S2). The low-temperature N₂ adsorption-desorption isotherms suggest that AC-0 contains nearly no micropores (Fig. S3). This result is confirmed by TEM studies, which show that AC-0 is composed mainly of randomly arranged graphitic domains (circled area in Fig. S4b). After activation, the intensity of the XRD (002) peak decreased gradually with increasing KOH amount (Fig. S5). At a KOH-to-carbon ratio of 3:1 (AC-3), this peak almost disappears and the low angle scattering signal increases, which indicating a high degree of disorder typical for microporous ACs [12]. TEM images confirm the influence of KOH on the structural transformation of ACs, where the graphic domains that exist in AC-0 evolve into porous carbon for KOH-activated AC samples (Fig. 1a–d and Fig. S4). AC-3 in particular consists predominantly of curved monoatomic layers of carbon, forming either slit-shaped, cylindrical, or conical pores between the interlaced flakes (arrows in Fig. 1d, Fig. S6). This transformation is schematically illustrated in Fig. S7. The TEM and FE-SEM (Fig. 1b and Fig. S8) images also show that AC-3 has uniformly distributed mesopores.

We analyzed the low-temperature N₂ adsorption-desorption isotherms of the ACs to determine their pore structure and pore size distribution (PSD) (Fig. 1e and f). The AC-1 and AC-2 samples show N₂ sorption isotherms reminiscent of Type I [15] with a pore width of ~0.8 nm based on a slit pore quenched solid density functional theory (QSDFT) model, indicative of a microporous material. AC-2 contains a larger volume of micropores than AC-1. In contrast, the AC-3 and AC-4 samples contain both micropores and mesopores, as shown by Type IV isotherms [16]. Specifically, the N₂ adsorption at low relative pressure (P/P₀) suggests the presence of micropores. Following the inflection point, the N₂ uptake continues to increase with P/P₀ and then terminates. This finite N₂ adsorption and the hysteresis between the N₂ adsorption and desorption isotherms indicate the presence of mesopores [17]. Analysis of the PSD suggests the dominant amount of micropores in AC-3, unlike AC-4. Table 1 lists the pore structure parameters of ACs. It shows that micropores contribute mainly to the SSA of AC-1 and AC-2, unlike in AC-3 and AC-4, where micropores and mesopores contribute
with different scan rates, the dependencies of specific capacitance on scan rate for (e) AC-1 and (f) AC-3 measured at different temperatures. 

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>AC-1</th>
<th>AC-2</th>
<th>AC-3</th>
<th>AC-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{\text{total}}$ (m² g⁻¹)</td>
<td>1197</td>
<td>2201</td>
<td>2797</td>
<td>2629</td>
</tr>
<tr>
<td>$S_{\text{micro}}$ (m² g⁻¹)</td>
<td>974</td>
<td>1349</td>
<td>1015</td>
<td>895</td>
</tr>
<tr>
<td>$V_{\text{total}}$ (cm³ g⁻¹)</td>
<td>0.684</td>
<td>1.259</td>
<td>2.482</td>
<td>2.461</td>
</tr>
<tr>
<td>$V_{\text{micro}}$ (cm³ g⁻¹)</td>
<td>0.446</td>
<td>0.672</td>
<td>0.607</td>
<td>0.539</td>
</tr>
</tbody>
</table>

* The QSDFT model is used to determine the pore-structure parameters of ACs [12].

significantly to high SSA (2797 m² g⁻¹ for AC-3). In addition, the hysteresis shown in AC-3 that the material mainly contains slit and cylindrical pores (Fig. S9).

2.2. Electrochemical performance

It is clear from the above discussions that the AC-1 and AC-3 have vastly different pore structures. Therefore, these two samples were employed for the study on the influence of temperature on supercapacitor performance.

We first used cyclic voltammetry to obtain the room-temperature characteristics of supercapacitors based on AC-1 and AC-3 in low-temperature electrolyte containing 1:1 ACN/DIOX mixture. The cyclic voltammograms (CVs) recorded at different scan rates (5–500 mV s⁻¹) exhibit a butterfly shape indicating a pure capacitive behavior (Fig. S10). Microporous carbons are known for achieving high capacitance at room-temperature due to desolvation of ions, but ions may be trapped in narrow pores [18]. These CVs show that the capacitance of the AC-1 gradually decreases with increasing scan rate, indicating poor rate capability. In contrast, there was only a slight change in the capacitance of the AC-3 even at 500 mV s⁻¹. The difference in the rate performance may be attributed to the presence of mesopores and larger micropores in AC-3, which allows for fast migration of ions [19,20]. These were further validated by galvanostatic charge-discharge studies (Fig. S11).

We then investigated the low-temperature electrochemical properties of the two materials. The CVs taken from −70 to 20 °C are shown in Fig. 2a and b. Unlike the specific capacitance of the AC-1, which decreases sharply when the temperature is decreased, there is only a minimal decrease in the specific capacitance of AC-3. The CVs of AC-1 deviate from the rectangular shape with decreasing temperature while those for AC-3 remain almost unchanged. Furthermore, when the effect of scan rate was evaluated at −70 °C (Fig. 2c and d), the CVs of AC-3 remain rectangular, while they become distorted with increasing scan rate for AC-1.

The significant differences in capacitance retention as a function of scan rate for the two materials when tested at different temperatures are evident in Fig. 2e and f. Even at sufficiently long charging time (i.e. at 5 mV s⁻¹), the specific capacitance of AC-1 decreases significantly with decreasing temperature resulting to only 12 F g⁻¹ at −70 °C, which is around one-tenth of the room temperature value. At 500 mV s⁻¹, the capacitance further decreases to 1 F g⁻¹. In comparison, the capacitance retention and the rate performance of AC-3 are exceptionally high even at low temperatures. At 5 mV s⁻¹, AC-3 retains a high specific capacitance of 164 F g⁻¹ at −70 °C (177 F g⁻¹ at 20 °C and 182 F g⁻¹ at 60 °C). Even at 500 mV s⁻¹, a very high capacitance of 112 F g⁻¹ is maintained at −70 °C. A 3:7 ratio of ACN/DIOX mixture further extended the low temperature operational limit of the AC-3 supercapacitor to −100 °C. A high specific capacitance of 164 F g⁻¹ at −100 °C was measured, which only slightly differed at 20 °C (173 F g⁻¹, Fig. S12). Furthermore, MeEt₃N·BF₄, with asymmetric structure, can be more easily dissolved than the highly symmetric TEA·BF₄. Even in pure DIOX, with a low dielectric constant, a very high salt concentration (≥1 mol L⁻¹) could be obtained. Therefore, even after holding at a low temperature for a long period of time (8 h at −100 °C), little salt recrystallization could be detected when this electrolyte (0.5 M MeEt₃NBF₄ in a 3 to 7 ACN-DIOX blend) was used.

Capacitance retention was measured over 10,000 cycles for the AC-3 (Fig. S13). It can be seen that the specific capacitance only decreased slightly with increasing cycle number, providing a capacitance retention of 99.3% at −60 °C. It is also noteworthy that the capacitance retention is reasonably high at 60 °C (84.9%), especially when compared to 20 °C (91.6%).

We used electrochemical impedance spectroscopy to further elucidate the difference in performance of the two AC-based supercapacitors. The Nyquist plots taken at different temperatures clearly show the superior performance of AC-3 over AC-1 (Fig. 3a and b). For AC-3, each Nyquist plot features a vertical line indicating close to the ideal capacitive behavior of the cell [21], which appears to be temperature independent. The equivalent circuit model of AC-3 measured at −70 °C is shown in Fig. S14. For AC-1, however, each Nyquist plot deviates from the
imaginary axis and skews to the right as the testing temperature is lowered. These results are consistent with the CV curves in Fig. 2a. Furthermore, although the high frequency region shows that the intercepts (Ohmic resistances) of the Nyquist plots are similar for AC-3 and AC-1, their mass transfer resistances (denoted as $R_{mt}$) exemplified by the semi-circles are quite different (Fig. 3a and b). Depressed semi-circles are considered representative of low $R_{mt}$ between the electrode and the electrolyte [22], as seen for AC-3 even at low temperatures (inset in Fig. 3b). For AC-1, however, the $R_{mt}$ increases greatly with decreasing temperature, which implies that ions become less likely to enter the pores of AC-1 at low temperatures. The $R_{mt}$ of AC-1 becomes much higher at $-70$ °C ($\approx 720 \Omega$) than at $20$ °C (1.7 $\Omega$), which confirms that ions barely enter the pores of AC-1 (Fig. S15). Bode plots of the same data (Fig. S16) for AC-3 show that the phase angles at low frequencies are close to $-90^\circ$ regardless of temperature, which further confirms the excellent capacitive behavior even at $-70$ °C. At a phase angle of $-45^\circ$, the frequencies ($f_0$) of 0.68 Hz at $20$ °C and 0.19 Hz at $-70$ °C correspond to time constants ($\tau_0$) of 1.47 and 5.26 s, respectively, which demonstrate the outstanding rate performance of AC-3 at room and low temperatures [16, 23].

Fig. 3c shows that the capacitance changes ($\Delta C / C_0$) of both devices measured at a scan rate of 5 mV s$^{-1}$ are quite different at different temperatures. Since the trend of the capacitance change versus temperature is very similar to that of $R_{mt}$, it can be deduced that the major difference between AC-1 and AC-3 at a low testing temperature is due to the $R_{mt}$ rather than the Ohmic resistance of the electrolyte (Fig. S17). This is further confirmed by the fact that ions could escape from the micropores in AC-1 at $-70$ °C (Fig. 3d).

### 2.3. Desolvation and pore geometry

The ions in an electrolyte exist in solvated form [24]. For EDLCs, the mechanism of ion desolvation during charging explains why carbon materials can have high charge storage capacities even when the size of their pores is smaller than that of the solvated ion [25,26]. This mechanism is seen for AC-1 when a high capacitance is attained even when its pore size (mainly $\approx 0.8$ nm) is smaller than a fully solvated ion ($\approx 1.01$–$1.32$ nm); its small pores accommodate the ions by the removal of their solvation shell. However, this mechanism proves to be temperature dependent for the ACs and electrolyte combination studied here. The decrease in capacitance with temperature for AC-1 suggests that ions can remain solvated (or partially solvated) at low temperature thereby preventing access to its small pores. These results contrast with those observed for AC-3, which has a pore size larger than 0.9 nm. Its high capacitance even at $-100$ °C shows that solvated and partially solvated ions can access its pores during charging. Therefore, although ion desolvation can play a role in achieving high capacitance for microporous materials as shown here and in the literature [24–27], it is also critical that the pore size of ACs match well with the size of solvated ions when the target application requires operation at low temperature.

Based on these results, we propose a temperature-dependent ion desolvation model using Arrhenius equation to determine the desolvation rate $k$:

$$k = A \cdot e^{-\frac{E_a}{k_b T}},$$

where $A$ is the pre-exponential factor, a frequency of attempt in desolvation, which can be estimated as the vibrational frequency $\nu$ of the solvent molecule bound to the MeEt$_3$N$^+$ ion ($\approx 10^{12}$ Hz in this work), $E_a$ is the activation energy for the desolvation process (binding energy between the solvent molecule and ion), $k_b$ is the Boltzmann constant and $T$ is the thermodynamic temperature in Kelvin.

Considering that the electrolyte is composed of ACN and DIOX, the MeEt$_3$N$^+$ ions can be solvated by two solvents simultaneously that leads to dynamic solvation shells with varied composition. The population of different solvation shells depends on their solvation energies and electrolyte composition. Table S1 shows that the donor numbers and viscosities of both solvents are close to each other, which indicates no
significant solvating priority of the two solvents in both thermodynamic and kinetic aspects. We investigated the effects of composition and population of different solvation shells on desolvation processes by considering two extreme cases where the ions are solvated by ACN and DIOX separately, and the desolvation behavior of other solvation shells is approximated as a combination of the two cases.

The solvation shell of MeEt₃N⁺ ions is constructed by the step-wise addition of solvating molecules, where the number of molecules added is referred to as the solvation number (SN), and the heat of reaction between that number of solvent molecules and MeEt₃N⁺ ion is defined as the solvation energy. Here, we only consider the first solvation shell where the solvation energy decrement is less than 0.2 eV with increasing SN. The calculated solvation energies and geometries of solvated ions with different SN are listed in Tables S2 and S3 (Methods section describes the calculations in detail).

Given the three different typical pore geometries in ACs (i.e. slit, cylindrical and sphere), their ability to accommodate the solvated ions may be analyzed based on their effective size. Tables S4 and S5 summarize the effective size of solvated ions that can be accommodated in each pore geometry for a given SN. These effective sizes are determined based on the following rationale: A slit-type pore can only confine a solvated ion in one direction, therefore the smallest axis in its geometrical size (Tables S2 and S3) determines the access of ions into the pores. In the case of cylinder-type pore, a solvated ion can be confined in two directions, therefore the second largest axis is the limiting factor during ion access. Lastly, the largest axis is used in the sphere-type pore because it can confine a solvated ion in all directions. In this case, if the pore size is determined, SN of the solvated ions in slit-type pore would be the largest, and consequently the lowest desolvation barrier is needed to overcome.

As the ACs are characterized predominantly by slit-type pore geometry (Figs. S6, S7 and S9), we plot the solvation energy versus SN along with the effective size of the solvated ions based on slit-type pore geometry (Fig. 4a and c). To move into a ∼0.9 nm slit-type pore, the effective size of solvated ion can be ∼0.7 nm after taking into account of the spaces above and below the solvated ions (at least 0.1 nm each) to avoid severe repulsion. According to Fig. 4a and c, the SN of inserted ion needs to be reduced to two if it is solvated by ACN, while the SN can be three in the case of DIOX. The maximum barrier energy to overcome is around 0.17–0.45 eV based on solvation shell composition (Tables S2 and S3). Using equation (1), the average desolvation time scale (τ) expressed as τ = 1/k is around 0.1 s even at −70 °C and at a maximum desolvation barrier of 0.45 eV. This very small τ indicates the capacitance is only slightly influenced by temperature (especially at low scan rate due to sufficient time for kinetic response) for ACs with slit-type pores of around 0.9 nm. However, when the slit-type pore size is less than 0.8 nm, it only allows the ions with an effective size around 0.6 nm or smaller to enter, and consequently its SN must be one or less (Fig. 4a and c). In this case, the minimum energy barrier to overcome is between 0.65 and 0.73 eV. At −70 °C, the τ of ∼3 h is required to overcome the minimum energy barrier of 0.65 eV, which indicates a sluggish desolvation process. However, at room temperature, the performance is expected to improve given its τ to be ∼1 s even with the high barrier energy of 0.73 eV. These calculations reveal that the ability of ions to penetrate pores of different size is temperature dependent, consistent with our experimental results (Fig. 2).

Therefore, achieving EDLCs with good performance at low temperature requires the pore shape and size of ACs be tailored towards the effective geometry of solvated ions in the electrolyte, such that the pore size should be at least larger than the ion cluster that can enter the pores during charging at low temperature (Fig. S18). These geometrical considerations are shown to be important here even when desolvation (or partial desolvation) is energetically favored during charging at the relevant temperature. This explains why high-surface area electrode materials with an open surface (carbon onions, nanotubes of porous graphene) can operate at low temperatures even with highly-viscous ionic liquid electrolytes [28,29], but microporous materials show no capacitance under the same conditions.

It is worthy to note that, in AC-3-based EDLC, although only a small change can be detected for CV curves measured at scan rate of 10 mV s⁻¹ at −100 °C (Fig. S12a), a sharp decrease is noticed when the scan rate

Fig. 4. Total energies and effective ion sizes (based on slit-type pore model) when MeEt₃N⁺ is solvated by (a) acetonitrile and (c) 1,3-dioxolane. The relation curves of average desolvolation time scale and solvation number at different temperatures for (b) MeEt₃N⁺ + acetonitrile system and (d) MeEt₃N⁺ + 1,3-dioxolane system.
increases to 100 mV s\(^{-1}\) (Fig. S12b). Galvanostatic charge/discharge curves measured at different temperatures also clearly show that the IR drop gradually increases with decreasing temperature (Fig. S19). Fig. S12d shows that all resistances increase gradually with decrease of temperature, but \( R_{\text{ext}} \) is not the key component of internal resistance. Therefore, the reduction in rate performance for AC-3 can be attributed to decreased ion transport. Further, it is noted that there are many mesopores exist in AC-3, the fabricated EDLC almost could be fully charged even when the scan rate increase to 30 V s\(^{-1}\) at room temperature (Fig. S20). Thus, it can be deduced that the reduction in rate performance is closely related to the conductivity of the electrolyte (Table S6). Here, we replaced DIOX with methyl formate in the ACN/DIOX mixture to increase electrolyte conductivity by virtue of lowering its viscosity. The result shows that the rate performance could be improved effectively (Fig. S21). Therefore, to further improve the rate performance of EDLCs at ultralow temperature, besides electrode materials, electrolyte with higher conductivity would be a great challenge.

3. Conclusions

Activated carbons with different pore sizes were used to determine a correlation between pore size and capacitance at low temperatures. The specific capacitance values of ACs with micropores are much different at room and subzero temperatures, even at a low scan rate of 5 mV s\(^{-1}\). On the contrary, the specific capacitance changes little with temperature for ACs with pores larger than a certain size. For AC-1, which has pores mainly smaller than 0.9 nm, the specific capacitance decreases sharply with temperature and it is only 12 F g\(^{-1}\) at \(-70^\circ\text{C}\), nearly one-tenth of the capacitance at room temperature. However, for AC-3 with sufficient volume of pores larger than 0.9 nm and high SSA, its specific capacitance reaches 164 F g\(^{-1}\) at \(-100^\circ\text{C}\). A temperature-dependent desolvation model is presented to explain the performance of carbon-based EDLCs at different temperatures. When the testing temperature decreases, the desolvation of ion clusters fail to occur and ion clusters bigger than the pores cannot participate in charge storage. As a consequence, the capacitance decreases to almost zero. The model and experimental validation presented here help elucidate the fundamental physics of desolvation of ion clusters, especially at low temperature. This understanding is critical for optimizing the pore structure of carbon materials for low-temperature tolerant supercapacitors.

4. Methods

4.1. Preparation of activated carbon materials

A two-step strategy was applied in the preparation of porous ACs (Fig. S1). The first step is a pre-carbonization process. 15 g soymeal was pre-carbonized in a furnace under nitrogen flow (~600 mL min\(^{-1}\)) at 400 \(^{\circ}\text{C}\) for 1 h resulting in a coke. The second step is an activation process. The produced coke (2 g) was ground with solid KOH at a KOH/coke weight ratio of X (where X = 0, 1, 2, 3, or 4). The resulting mixture was placed in a nickel crucible into a tubular furnace, and then heated to 800 \(^{\circ}\text{C}\) (at 5 \(^{\circ}\text{C}\) min\(^{-1}\)) for 1 h under argon flow (~200 mL min\(^{-1}\)). The carbon materials were washed with excess 1 M HCl solution and deionized water to remove any impurities. The resultant AC was dried at 80 \(^{\circ}\text{C}\) overnight and annealed under vacuum at 800 \(^{\circ}\text{C}\) for 2 h. The samples are denoted as AC-X, where X stands for the weight ratio of KOH/coke.

4.2. Materials characterization

The microstructure of the carbon materials was characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and low-temperature N\(_2\) sorption techniques. XRD patterns were collected by Rigaku D/Max-2500 powder diffractometer with Cu-K\(_a\) radiation (\(\lambda = 0.154 \text{ nm}\)) operated at 40 kV and 200 mA. TEM was performed using a JEM 2010 TEM equipped with an imaging filter (Gatan GIF) at 200 kV. The \(N_2\) adsorption and desorption isotherms were measured at 77 K on a Quantachrome Autosorb-iQ3. All samples were outgassed in vacuum at 200 \(^{\circ}\text{C}\) for 12 h. Quenched solid density functional theory (QSDFT, assuming the pores are slit/cylinder shaped) was used to determine the pore size distribution, pore volume and specific surface area (SSA). According to convention, macropores, mesopores, and micropores are described as those having diameters >50 nm, between 2 and 50 nm, and <2 nm, respectively.

4.3. Electrode preparation and electrochemical measurements

An 88 wt % AC was mixed with 4 wt % carboxymethyl cellulose (CMC), 4 wt % styrene-butadiene rubber (SBR) and 4 wt % carbon black in deionized water to make a homogeneous slurry. The slurry was cast on aluminium foil with a thin carbon coating layer using the doctor blade method, followed by vacuum drying overnight at 120 \(^{\circ}\text{C}\). The mass loading of the electrode was \(-1.5 \text{ mg cm}^{-2}\). All electrochemical investigations were carried out in a symmetrical two-electrode button cell (Fig. 1). The electrolyte used was 0.5 M MeEt3NBF4 in a 1:1 or 3:7 v/v mixture of acetonitrile (ACN) and 1,3-dioxolane (DIOX). Porous PP (Celgard 3500) was used as separator. Before each measurement, the assembled capacitor was left to rest overnight to ensure that the electrodes are thoroughly wetted by the electrolyte. The electrochemical performance of the AC-based supercapacitors were characterized by cyclic voltammetry (CV) and galvanostatic charge/discharge tests. The employed potential range was between 0 and 2.5 V, the scan rates were 5-500 mV s\(^{-1}\) and current densities were 5-30 A g\(^{-1}\). Electrochemical impedance spectroscopy (EIS) was measured from 10\(^{-2}\)-10\(^{5}\) Hz using a 5 mV peak voltage for the open circuit potential. All electrochemical measurements were performed on a CHI660E electrochemical workstation. The performance of the EDLCs at different temperature was measured in a high/low temperature test chamber (GP/T-150, Guangpin test equipment manufacturing Co., Ltd.).

The gravimetric capacitance of a single electrode based on the CV curves (\(C_{\text{CV}}\)) was calculated according to the following equation:

\[
C_{\text{CV}} = 2 \int_0^U \frac{I(U)dU}{m(V(b-a))},
\]

where \(I(U)\) and \(V\) are the discharging current and the scan rate, respectively, \(m\) is the mass of active material on one electrode and \(a (0 \text{ V})\) and \(b (2.5 \text{ V})\) are the initial and final voltage during discharge, respectively.

The gravimetric capacitance of single electrodes, based on galvanostatic charge/discharge curves (\(C_{\text{gal}}\)), were also calculated using the following equation:

\[
C_{\text{gal}} = \frac{2I_{\text{del}}}{m3V},
\]

4.4. Modeling and theoretical calculations

When the solvated ion meets smaller pore, it will overcome solvation energy to remove outer solvents to meet the corresponding pore size. Thus, Arrhenius equation might be suitable to determine the desolvation rate of solvated ions at certain energy and temperature. The geometry and the total energy of solvated ions were calculated using density functional theory (DFT), which was implemented in the Vienna ab initio simulation package (VASP) [30] by adopting the projector-augmented wave (PAW) method [31]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) function [32] was used to describe the exchange-correlation interactions. The cut-off energy was 450 eV, and the criteria of convergence for energy and force were 10\(^{-4}\) eV and 10\(^{-2}\) eV Å\(^{-1}\), respectively. A cubic supercell with a size \(L\) of 30 Å was adopted to optimize the molecules. For charged ions with solvation shell, the leading errors from neutralizing background charge [33] was corrected by
\[ \frac{e^2 q^2}{k_B T} \] (4)

where \( q \) is the net charge of the supercell, \( a \) is the Madelung constant of a point charge \( q \) in a homogeneous background charge \( -q \), and \( \epsilon (\sim 20) \) is the dielectric constant of the solvent, which was estimated as the volumetric average of the ACN and DIOX dielectric constants (Table S1). The solvation energy was calculated using the following formula:

\[ \Delta E = E(A^+ nB) - E(A^+) - nE(B), \] (5)

where \( E(A^+ nB), E(A^+) \) and \( E(B) \) denote the total energy calculated from DFT of the solvated ion, naked ion and solvent molecule, respectively and \( n \) is the solvation number.

The vibrational frequency \( (\nu) \) was calculated using the harmonic model as follows:

\[ \nu = \frac{1}{2\pi} \sqrt{\frac{k_j}{m}}, \] (6)

\[ k_j = \frac{\Delta E}{\Delta x^2}, \] (7)

where \( k_j \) is the spring constant, \( \Delta E \) is the calculated binding energy change when the solvent molecule deviates from the equilibrium binding distance by \( \Delta x \), and \( m \) is the mass of a solvent molecule. In this work, \( k_j \) is about 9.5 N/m, and the frequency is estimated as \( 10^{-12} \text{Hz} \).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ensm.2019.02.016.

References