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Ionic liquid electrolytes in electric double layer capacitors

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ABSTRACT Electric double layer capacitors (EDLCs), which store free charges on the electrode surface *via* non-Faradaic process, balanced by the electric double layer on the electrolyte side, exhibit excellent cycle stability and high power density. Though EDLCs are considered as promising energy storage devices, the charges stored on the electrode surface in EDLCs are much lower than those in batteries. Ionic liquids (ILs), as a new type of electrolytes in EDLCs, are capable to deliver high energy density, due to their excellent physicochemical properties and wide electrochemical window. In this review, we focus on the widely studied IL electrolytes for EDLCs, including pure ILs, IL/IL binary electrolytes, IL/organic solvent mixtures, as well as functionalized ILs, with attention on the relationship between the structures of different IL-based electrolytes and the energy storage properties in EDLCs. For imidazolium- and ammonium-based IL electrolytes which are most widely studied in EDLCs, the former generally have higher gravimetric specific capacitance, while the latter exhibit wider electrochemical window. The modifications of functional group substituted can be an effective strategy to enhance the gravimetric specific capacitance of the latter and thus improve the energy density of EDLCs.

Keywords: ionic liquids, electric double layer, capacitive performance, energy density, modification of IL electrolytes

INTRODUCTION

Ionic liquids (ILs), as “designer solvents”, are composed of bare ions with organic cations and organic or inorganic anions, which are liquids at room temperature. Most cations and anions are depicted in Fig. 1. ILs with remarkable physicochemical and electrochemical properties, such as high thermal stability, low vapor pressure, and wide electrochemical window, are considered as

promising electrolytes for energy storage in electric double layer capacitors (EDLCs) [1–3]. In EDLCs, charges are stored on the 2-dimensional electrode surface *via* non-Faradaic process, which is considerably different from the batteries in which charges are stored in 3-dimensional electrode *via* Faradaic process. The charging/discharging process in EDLCs is accompanied by the formation of electric double layer (EDL) in the electrolyte, while that process in batteries is generally accompanied by the intercalation/deintercalation and diffusion of ions in the electrode material [4,5]. Thus, EDLCs are capable of delivering higher power density with faster charging/discharging rate than batteries. Additionally, the non-Faradaic process makes no degradation of electrode materials in EDLCs, and theoretically infinite cycling. Thus, EDLCs are able to provide excellent cycling stability (> 500,000 cycles) [6–8] and high power density (up to 10 kW kg^{−1}) [7,9]. On the other hand, the charges stored on electrode surface in EDLCs are much lower than those in batteries. The relatively low energy density of EDLCs makes them difficult to replace batteries as energy storage devices in most practical applications at current stage [10].

The energy density of EDLCs is calculated by $E=1/2CV^2$, in which C is the capacitance of EDLCs and V is the cell voltage. Thus, the energy stored in EDLCs increases as the square of V . Compared with the electrochemical window of aqueous electrolytes of ~1 V [11–14] or organic electrolytes of ~2.7 V [15], ILs exhibit wider electrochemical window, which can be up to 5 V [16]. Fig. 2 compares the cell voltage of aqueous electrolytes, organic electrolytes, and ILs, in which [C₂MIm]BF₄ shows wider cell voltage (~3.5 V) with higher energy density [17]. Thus, EDLCs with IL electrolytes have received

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Figure 1 Chemical structure of several common cations and anions of ILs. Cations: (a) 1-alkyl-(2,3)-(di)methylimidazolium ([C_nMIm]⁺, [C_nMMIm]⁺), (b) 1-alkyl-1-methylpyrrolidinium ([Pyr_{1,n}]⁺), (c) spiro-(1,1')-bipyrrolidinium ([SBP]⁺), (d) 1-alkyl-1-methylpiperidinium ([Pip_{1,n}]⁺), (e) tetraalkyl ammonium and phosphonium ([N_{k,lmn}]⁺, [P_{k,lmn}]⁺); Anions: (f) tetrafluoroborate and tetracyanoborate (BF₄⁻ and B(CN)₄⁻), (g) hexafluorophosphate and tris(pentafluoroethyl)trifluorophosphate (PF₆⁻ and FAP⁻), (h) bis(fluorosulfonyl)imide and bis(trifluoromethylsulfonyl)imide (FSI⁻ and TFSI⁻), (i) trifluoromethanesulfonate (TF⁻), (j) dicyanamide (DCA⁻).

Figure 2 Comparison of (a) cell voltage and (b) Ragone plots in KOH, LiPF₆/EC/dimethyl ether (DME), and [C₂MIm]BF₄. Reprinted with permission from Ref. [17]. Copyright 2013, Royal Society of Chemistry.

considerable attention, and are proved to be as energy storage devices with not only high power density and cycle stability, but also high energy density.

Apart from the cell voltage V , the energy density of EDLCs also grows with capacitance C , which is a complicated function that depends on electrodes, electrolytes, and the EDL thus formed. Nevertheless, it can be casted with the well celebrated Helmholtz model [18], i.e., $C = \frac{\epsilon\epsilon_0 A}{d}$, in which ϵ_0 denotes the vacuum dielectric permittivity, ϵ denotes the relative dielectric permittivity of electrolytes, A is the effective specific surface area (SSA) of electrode that is accessible by electrolyte ions,

and d is considered as the effective EDL thickness, respectively [19]. For EDLCs in which the electrode charges are balanced by a thin EDL layer, ϵ can be represented as optical dielectric permittivity (ϵ_∞) which is generally less than 2, contributed by the electronic polarization. Thus, the practical strategies of manipulation of EDLCs for higher C are increasing A of the electrode and decreasing d of EDL.

A highly effective SSA can potentially ensure more charges storage on the electrode surface [20]. The pore size can also play an important role in determining the accessible surface for electrolyte ions to form EDLs [21]. Thus, the pore size distribution of electrode is important

to improve the capacitive performance [22–24]. Additionally, the SSA is also greatly related to the pore geometry, such as slit, cylindrical and spherical [25]. The wettability of electrodes with IL electrolytes can facilitate ion diffusion in porous structure, and increase ion fluidity for EDL structure [26]. Therefore, the optimization of specific surface area, pore size distribution and conductivity of electrode materials can contribute to high specific capacitance, high stability and fast charging/discharging process of EDLCs, and thus towards higher energy density as well as higher power density [27–29]. Additionally, an optimized EDL thickness d can screen the electric field on the electrode more efficiently and thus increase C . Lately, the incorporation of surface functional groups into electrodes is used to optimize intermolecular interactions between porous electrodes and electrolyte ions, which can improve pore ionophilicities and influence the dynamics of electrolytes [30–34]. However, this incorporating may introduce pseudo-capacitance and lead to some shortcomings, such as shortening cycling life and narrowing electrochemical window [35,36]. It should be emphasized that the rich fundamental thermodynamics is involved in EDL, which has been studied over the past 100 years [37,38], and is still an active field nowadays [39].

On the other hand, assuming ILs as concentrated electrolytes, anomalously long screening length demonstrates an important characteristic in them [40,41]. The strong ionic interaction of ILs results in the oscillation layering of counter-ions and co-ions (overscreening ef-

fect), which increases the thickness of ionic layers and further reduces the capacitance [42]. ILs diluted with polar solvents and functionalized with organic group are proposed as efficient strategies to reduce the overscreening effect. Some functionalized ILs and common organic solvents are described in Fig. 3.

In this review, we focus on the widely studied IL electrolytes for EDLCs, including pure ILs, IL/IL binary electrolytes, IL/organic solvent mixed electrolytes, as well as functionalized ILs, with attention on the relationship between the structures of electrolyte ions and the energy storage properties in EDLCs.

ELECTRIC DOUBLE LAYER AND DIFFERENTIAL CAPACITANCE

Fundamental understanding of EDL structures dependent on the electrolyte ions is important for facilitating the applicability in EDLCs. Capacitance-potential relationship, namely, differential capacitance (C_d) is probed to better understanding the EDL structure and properties of IL/electrode interface [43–45]. Using Helmholtz model, the voltage-dependent EDL thickness can be probed as $\frac{1}{d(V)} = \frac{C_d(V)}{\epsilon\epsilon_0}$. The measured C_d is equivalent to the effective EDL thickness d , which is a function of the polarized potential.

Experimentally, EDL structures may be probed by C_d using electrochemical impedance spectroscopy (EIS) technique. An impedance model for SCs consists of three regions: (i) the semi-circle at high frequency indicates the

Figure 3 The structure of functionalized cations and common organic solvents. Functionalized cations: (a) 1-alkoxyalkyl-(2,3-di)methylimidazolium ($[C_{nOm}MIm]^+$, $[C_{nOm}MMIm]^+$), (b) 1-alkylcarboxyalkyl-(2,3-di)methylimidazolium ($[C_{nCOM}MIm]^+$, $[C_{nCOM}MMIm]^+$), (c) 1-alkoxyalkyl-1-methylpyrrolidinium ($[PyT_{1,nOm}]^+$), (d) ether-functionalized tetraalkyl ammonium and phosphonium ($[N_{klm(nOv)}]^+$, $[P_{klm(nOv)}]^+$). Organic solvents: (e) ethylene carbonate (EC), (f) propylene carbonate (PC), (g) 1,2-dichloroethane (DCE), (h) acetonitrile (AN), (i) adiponitrile (ADN), (o) dimethyl carbonate (DMC), (p) dimethyl sulfoxide (DMSO).

charge transfer resistance formed at the electrolyte/electrode interface; (ii) the mid-frequency Warburg impedance for EDLCs may result from the surface diffusion of the adsorbed ions and the diffusion within narrow pores; (iii) low-frequency capacitive behavior [46]. In comparison to complex impedance (Nyquist) representation, complex capacitance (Cole-Cole) plot is suggestive for understanding the charging/discharging with the separated capacitive processes. Fig. 4a shows a schematic EDL structure against a negatively charged planar electrode. Correspondingly, an ideal resistor-capacitor (RC) series circuit is adopted to represent EDL formation, along with the relaxation process appearing in the Cole-Cole plot shown in Fig. 4b, in which the complex capacitance is used to describe the EDL charging processes. As shown in Fig. 4c and d, $C_d(V)$ clearly demonstrates that two capacitive processes take place on sub-millisecond time scale for the fast capacitive process and sub-second time scale for the slow capacitive process,

respectively. In Fig. 4c, the Cole-Cole spectrum was fitted by $C(V, f) - C_\infty = \sum_{n=1}^3 \frac{C_{\text{Cole},n} - C_\infty}{1 + (j2\pi f\tau)^{\alpha_{\text{Cole},n}}}$, in which $C_\infty \cong 0$ denotes bulk capacitance which is negligible, and $0 < \alpha_{\text{Cole},n} \leq 1$, where $\alpha_{\text{Cole},n}=1$ denotes the ideal capacitance process [47]. It is notable that the fast capacitive process is commonly attributed to the Debye relaxation for the EDL charging [48,49], while the slow process is still under debates. For instance, the slow process was described as a slow Havriliak-Negami (HN) relaxation in Fig. 4d [49]. Roling *et al.* [47,48,50–52] suggested the slow process on the time scale of second may be related to structural reconstructions of the metal electrode surface and/or ion redistributions in the strongly bound ion-layer, which has been demonstrated by *in-situ* scanning tunneling microscopy (STM) [53,54]. Anderson *et al.* [55] attributed the slow process to the adsorption capacitance of the ions, while Pajkossy *et al.* [56] attributed the slow process to the dynamics of anions/cations replacement in the com-

Figure 4 (a) EDL for a negatively charged planar electrode at fixed voltage (V) and the accumulated charge (q) at time t , which is balanced by counter-ions in electrolytes. (b) RC series circuit representation (inset) of EDL in (a), in which C_d denotes EDL capacitance, and R_s denotes the solution resistance. (c) Complex capacitance of [Pyr_{1,4}]TFSI/Au(111) electrode measured at $V = -0.9$ V vs. Fc^0/Fc^+ with EIS. Reprinted with permission from Ref. [47]. Copyright 2012, Royal Society of Chemistry. (d) Complex capacitance of [C₄MIm]PF₆/Pt electrode measured at $V = -0.5$ V vs. Ag wire with EIS. The inset of (d) shows $C_d(V, f)$ with both EIS measurements (dot) and fits (solid line). Note that for ideal RC series in (b) with only Debye relaxation, C_{Debye} is constant across the whole frequency window (dashed line). Reprinted with permission from Ref. [49]. Copyright 2018, Elsevier.

compact layer. Although the physical models proposed by Roling *et al.* and Pajkossy *et al.* are based on general knowledge about electrochemical interface in ILs, their validation requires more precise structural information obtained by other approaches. Based on the results of *in-situ* STM and atom force microscopy (AFM), Li *et al.* [57] revealed that the EDL was formed by three charged interior layered structures, while strong adsorption was absent in the interface. Meanwhile, an electric equivalent circuit involving different capacitance processes of different time scales was proposed, and the slow process may be due to the hindrance of reorientation and/or redistribution of ions in the more ordered and robust inner layer region. Though the origin of the slow capacitive process is still not clear, some recent studies attributed the fast capacitive process to the EDL formation [49,52].

Fig. 5 shows the C_d -potential relationship and relaxation time-potential relationship of $[C_2MIm]TFSI$ and $[C_4MIm]PF_6$ on Au electrode, in which C_d was obtained by fitting against the full EIS spectra. The range of C_d of about $4\text{--}20\text{ }\mu\text{F cm}^{-2}$ is typical for most ILs [58]. The

variation of C with voltage reflects the different potential dependent EDL structure, or the voltage dependent EDL thickness. Since $\alpha > 0.9$ at all voltage, the fast capacitive process, which is attributed to the formation of EDL, is close to the ideal Debye relaxation, and may be represented by RC series in Fig. 4b. It is also notable that C_d curves of the two ILs in Fig. 5 are in the same range, while τ_{Cole} of $[C_4MIm]PF_6$ is an order of magnitude higher than that of $[C_2MIm]TFSI$. Since $\tau = R_s C_d$, the solution resistance of R_s of the former is an order of magnitude higher than that of the latter, and the charging/discharging of $[C_2MIm]TFSI$ is much faster than that of $[C_4MIm]PF_6$. Thus, much information of EDL is probed with EIS.

Fig. 6 shows the C_d of widely studied imidazolium- and ammonium-based ILs ($[C_2MIm]BF_4$, $[C_2MIm]TFSI$, $[N_{1114}]TFSI$, $[N_{1888}]TFSI$), the ether group functionalized ammonium-based IL ($[N_{122(102)}]TFSI$), as well as IL/organic solvent mixtures containing imidazolium-based IL ($[C_2MIm]TFSI$) and acetonitrile (AN) with glassy carbon (GC) electrode. It is notable that GC electrode may be

Figure 5 C_d curves of $[C_2MIm]TFSI$ and $[C_4MIm]PF_6$ on Au electrode. C_d was fitted against complex capacitance of full EIS spectrum with a Cole-Cole relaxation (Fig. 4c) and a constant phase element (CPE) for low frequency region ($<20\text{ Hz}$), and $C_d = C_{\text{Cole}}$ for the fast Cole-Cole relaxation of sub-millisecond time scale. The top plots show α_{Cole} is in the range between 0.9 and 1.0, which is close to the ideal Debye relaxation ($\alpha=1$); the middle plots show that the Cole-Cole relaxation is on the sub-millisecond time scale; the bottom plots compare the C_d reported by the same authors in two different studies. Reprinted with permission from Ref. [52]. Copyright 2018, American Institute of Physics.

Figure 6 Differential capacitance measured on the GC electrode using different types of IL electrolytes. (a) $[N_{1114}]TFSI$ with a 5 V electrochemical window and (b) $[C_2MIm]TFSI$ with a 4.3 V electrochemical window. The measurements (dots) were performed with complex capacitance of EIS spectrum based on the frequency range of 100 mHz–500 kHz. The point of zero charge (PZC) is denoted by the arrow. Reprinted with permission from Ref. [16]. Copyright 2018, the Royal Society of Chemistry. (c) C_d of $[C_2MIm]BF_4$, $[N_{122(102)}]TFSI$ and $[N_{1888}]TFSI$, measured with single frequency EIS at 200 Hz. Reprinted with permission from Ref. [61]. Copyright 2009, American Chemical Society. (d) C_d of $[C_2MIm]TFSI/AN$ mixtures with different mole concentrations of $[C_2MIm]TFSI$, measured with single frequency EIS test at 46 Hz. Reprinted with permission from Ref. [62]. Copyright 2015, American Chemical Society. The solid curves in (a) and (b) denote the fitting against a mean-field theory [63].

considered as a prototypical electrode for the EDLCs with porous carbon electrode but flat electrode surface to explore the EDL on the electrolyte side for the C_d measurement. Thus, EDL structure is manifested in the C_d curves, and it is notable that different sizes and chemical natures of cations and anions of ILs play a role in the formation of EDL. Here, caution should be addressed on the C_d curves reported by different research groups, such as the manner to determine C_d , purity and compositions of ILs and a different electrochemical window that the measurements were performed. Such ambiguity is reflected in comparing C_d of neat $[C_2MIm]TFSI$ in Fig. 6b (camel-shaped) and d (U-shaped). Such shapes originate from the nature of different compositions of ILs on building EDL in response to the electrode polarization [59,60]. In Fig. 6b, $[C_2MIm]TFSI$ exhibits a higher capacitance at anodic polarization, which is screened by anion, $TFSI^-$. In contrast, $[N_{1114}]TFSI$ displays a higher capacitance at cathodic polarization than anodic polarization in Fig. 6a. Comparing Fig. 6a and b, the C_d in

$[C_2MIm]^+$ is higher than that in $[N_{1114}]^+$, although both with $TFSI^-$ anion. The results indicate that the cation plays an important role in determining the anion packing density on the anodic electrode surface. In addition, the ion size effect on the C_d can also be revealed in Fig. 6c, in which C_d of $[C_2MIm]BF_4$ is much higher than that of $[N_{1888}]TFSI$ with large cationic size. On mixing with organic solvent AN, C_d rises dramatically, as shown in Fig. 6d, owing to the effective dispersions of single ions in the electrolyte solution.

Table S1 summarizes the C_d of different ILs on different electrodes (Au, Pt, Hg, GC). It should be kept in mind that single EIS frequency measurement at low frequency seems to overestimate C_d , as shown in the inset of Fig. 4d, due to the reason that Debye relaxation associated with EDL charging/discharging process completes in sub-millisecond time scale. Though there is inconsistency in C_d even for the same ILs with the same electrodes, the general trend can be still derived from it. Nowadays, most ILs in capacitance studied can be classified as (1) 1,3- or

1,2,3-alkylimidazolium; and (2) tetraalkyl ammonium (including pyrrolidinium) or phosphonium, with different anions, such as PF_6^- , BF_4^- and TFSI^- (Fig. 1). Apart from that, there are also many studies on IL/IL mixtures, IL/organic solvent mixtures, and cationic functionalized ILs such as ether-substituted imidazolium and ammonium cations. The asymmetric C_d shape is reflected on the extreme values on the positive or negative polarizations, and C_d of most ILs is in the range of $4\text{--}20\text{ }\mu\text{F cm}^{-2}$. Imidazolium-based ILs are the most studied class of ILs in capacitance with wide electrode chemical window, up to 4.5 V for $[\text{C}_2\text{MIm}]\text{TFSI}$ on Pt electrode [64]. Ammonium-based IL ($[\text{N}_{1114}]\text{TFSI}$) has the widest electrochemical window up to 5.7 V on GC electrode [16]. Indeed, ammonium-based ILs, with wide electrochemical windows, are appropriate candidates to deliver high energy according to $E = 1/2 CV^2$. It is notable that IL/organic solvent mixtures generally have higher C_d than neat ILs, but limited by its relatively narrow electrochemical window ($<3\text{ V}$). In addition, the C_d mainly characterizes the capacity of charge storage in response to a perturbation of applied polarization potential. The C_d plots possess detailed information of EDLs as a function of the polarized electrode potential, such as the feature of the overscreening effect and crowding effect. Compared with the planar electrodes, porous electrode materials possess diverse and irregular geometric structure, resulting in the distinct feature for the EDLs charging processes hidden. Thus, for porous electrodes, the integral capacitance (C_i) is the most important observable of EDLCs, which characterizes the capacity of charge storage within an applied electrode potential vs. PZC. Therefore, both differential capacitance and integral capacitance characterize the capacity of charge storage, where $C_i = \int_{\text{PZC}}^V C_d dV / \int_{\text{PZC}}^V dV$. In brief, fundamental understanding of EDL structure by C_d curves with EIS technology can be used to improve the electrochemical performance of EDLCs with porous electrodes.

CAPACITIVE PERFORMANCE FOR IL-BASED EDLCs

ILs with electrode materials for high performance of EDLCs

Those carbon materials with high SSA in Table S2, including graphene, activated carbon, carbide-derived carbon, are widely used in EDLCs, which can enhance energy density. The experimental results and the related SSA (in Table S2) further confirm that charge storage in

higher SSA leads to enhanced capacitive performance, and then provides higher energy density. Compared with the planar electrodes, the charging mechanisms of EDLCs based on porous carbons are more complex, such as counter-ions adsorption, co-ions desorption and ion exchange in the EDL layers adjacent to the carbons [46,65,66]. For example, the charge storage in sub-nanopores performs a function of the electrode voltage, which is mainly achieved by ion exchanging from co-ions desorption and counter-ions adsorption, entirely governed by co-ions desorption [67]. Meanwhile, the C_i is more appropriately instead of C_d for EDLCs in contact with porous electrodes. An IL-based EDLC is composed of two porous carbon electrodes with high SSA, isolated by a separator and impregnated with electrolytes [68]. A scheme of such symmetric EDLC is depicted in Fig. 7a, along with a representative 3-dimensional porous graphene material in Fig. 7b. With a cell voltage (V) applied between the electrodes, cations of electrolytes accumulate on the cathode surface, while the anode surface attracts anions. Hence, an EDLC is equivalent to two capacitors of C_+ and C_- in series, with C_+ and C_- for the capacitance of the anode and cathode respectively, i.e., $\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-}$.

The charges stored on anode (Q_+) and cathode (Q_-) may be calculated *via* integration of C_d for the anodic and cathodic branch individually, i.e., $Q_{\pm} = \int_{\text{PZC}}^{V_{\pm}} C_d(V') dV'$, in which $C_{\pm} = \frac{Q_{\pm}}{V_{\pm} - \text{PZC}}$ [52]. Since C_d is asymmetric due to the different chemical nature of cations and anions, C_+ is not necessarily equal to C_- . On the other hand, the stored charges are balanced, i.e., $Q_+ = -Q_-$, so that the voltage on anode (V_+) and cathode (V_-) are not necessarily symmetric with respect to the bulk voltage, though the assembly of EDLC is symmetric.

It is notable that the areal specific capacitance (C_{SSA} , Table S2) does not indicate a linear relationship between the gravimetric specific capacitance and the increased SSA. The reason is that pore size distribution (PSD) is also important in determining the energy density of EDLCs, besides SSA [69]. Chmiola *et al.* [70] demonstrated that the capacitance firstly decreased with decreasing the pore size to less than twice of the counter-ion size, and then increased rapidly with further decreasing the pore size to approach to the counter-ion size, as shown in Fig. 7c. C_{SSA} normalized by the SSA depended on the pore size of electrode materials in $[\text{N}_{2222}]\text{BF}_4/\text{AN}$ electrolytes. The pores size comparable to that of the counter-ions facilitated to enhance the areal specific capacitance, since the desolvated counter-ions by the lim-

Figure 7 (a) A scheme of a symmetric EDLC with porous carbon electrodes, left: cathode, right: anode, vertical dashed line: separator. The red line denotes potential drop from anode to cathode. (b) A representative 3-dimensional model of porous graphene-based material with high SSA. Reprinted with permission from Ref. [79]. Copyright 2013, Nature Publishing Group. (c) Dependence of areal specific capacitance on the pore size of electrode composed of carbon nanotubes of different diameters with $[N_{2222}]BF_4/AN$ electrolytes. This study highlights the importance of PSD in the capacitance performance. Reprinted with permission from Ref. [70]. Copyright 2006, American Association for the Advancement of Science. (d) Schematic diagrams of EDL charging in micropores, mesopores, and macropores. Reprinted with permission from Ref. [71]. Copyright 2008, Wiley.

ited pore width may allow closer approach of the counter-ions to the electrode surface, resulting in the decreasing of EDLs thickness d . Furthermore, the pore curvature of electrodes also affects the capacitance of EDLCs [71]. When the charge stored in the micropores (<2 nm), counter-ions can link up along the pore axes, while the counter-ions can be adsorbed on the pore walls in mesopores (2–50 nm), as shown in Fig. 7d. In the macropores (>50 nm), the macropores electrode/electrolyte interface can be approximately by an EDL (in Fig. 7d). Namely, the pore geometry plays a significant role in the charge storage of EDLCs. By assuming that the pores are cylindrical, the counter-ions enter the micropores and link up to form electric wire-in-cylinder capacitor, which rationalizes an anomalous increase of C_{SSA} in sub-nanometer pore regime III of Fig. 7c. For mesopores, counter-ions enter pores and approach near the electrode surface to form electric double-cylinder capacitor, while

the pore curvature effect is negligible for macropores. In addition, the C_{SSA} exhibits oscillatory behavior as a function of pore size with a broad distribution, since the measured C_{SSA} is averaged over pore size [72]. In contrast to the above mentioned endohedral nanopores, counter-ions approach the external surfaces of 0-dimension onion-like carbon (OLC) and 1-dimension carbon nanotubes (CNTs) to form exohedral electric double-sphere capacitor and exohedral electric double cylinder capacitor, respectively [73]. Feng *et al.* [74,75] studied the effects of electrode curvature on the charge storage in EDLCs based on ILs. They found that the C_{SSA} increased with increasing curvature and decreasing OLC size, in agreement with the theoretical prediction [73].

On the other hand, electrolytes also play an important role in the charge storage of EDLCs, and it is meaningful to understand the dynamics of charge storage of EDLCs. It was confirmed that the correlation between the elec-

trolyte and the electrode is important in the IL-based EDLCs, such as a π - π stacking structure formed by imidazolium-based ILs in contact with graphene electrode [76,77]. Especially, the semi-infinite diffusion within the bulk electrolyte does not affect the charge storage of EDLCs, while the main diffusion process in such electrostatic adsorption should be the surface diffusion near the electrode [46]. Jo *et al.* [78] investigated the charging dynamics of cyano-based ILs for EDLCs by molecular dynamics (MD) simulations. They revealed that the C_d

maxima of all liquids resulted from the respective anions desorption. They subsequently reported that the charging dynamics of EDLCs was largely dependent on the co-ions desorption by MD simulations [76].

Influence of ionic composition of ILs on the performance

Fig. 8a–c demonstrate the effects of cations containing various alkyl side chain lengths and types on gravimetric specific capacitance. Owing to the increased size of cations, the gravimetric specific capacitance decreases with

Figure 8 Comparisons of gravimetric specific capacitances using different IL electrolytes. (a–c) The effect of cationic sizes and types on the C at different current densities. The cycle stability of (a) alkyl chain length in imidazolium-based ILs, (b) different types of cations with ring structure and (c) alkyl chain length in tetraalkyl ammonium-based ILs measured at a current density of 1 A g⁻¹. Reprinted with permission from Ref. [97]. Copyright 2016, American Chemical Society. (d) The effect of anion types on the electrochemical windows and charging/discharging processes at a current density of 1 A g⁻¹. Reprinted with permission from Ref. [83]. Copyright 2014, Wiley. (e) Cycle performance and galvanostatic charging/discharging curve (inset) for [C₂MMIm]BF₄/AN mixed electrolytes under different concentrations at a constant current density of 0.02 A g⁻¹ in the cell voltage from 0.0 to 2.7 V. Reprinted with permission from Ref. [86]. Copyright 2019, Springer. (f) The effect of ether-functionalization on improving gravimetric specific capacitance for pyrrolidinium-based ILs at a current of 2.5 mA cm⁻². Reprinted with permission from Ref. [90]. Copyright 2016, Elsevier. The capacitance in (a–c) was reported as single electrode capacitance, while the capacitance in (f) was reported as cell capacitance.

the longer alkyl side chain. The reason may be that the sieving effect of electrolyte ions decreases the concentration of counter-ions inside the pore with increasing the cationic size. On the other hand, as the increasement of alkyl tail in cations, the volumetric limitation reduces the favorability of the cationic orientation in the pore. The increased cationic size also decreases the utilization of the accessible surface area. Thus, $[C_2MIm]TFSI$ exhibits the highest gravimetric specific capacitance compared with other imidazolium-based ILs with the common anion as shown in Fig. 8a. For ammonium cations, pyrrolidinium-based ILs exhibit a higher capacitance than tetraalkyl ammonium-based ILs. Spiro-(1,1')-bipyrrolidinium cation ($[SBP]^+$, in Fig. 1c) has attracted interest in enhancing capacitance, owing to the increased pore accessibility and ionic packing density by the decreased ionic size [80–82]. For imidazolium-based ILs of $[C_2MIm]^+$ with different anions in Fig. 8d, it can be seen that BF_4^- and $TFSI^-$ anions can be operated with higher cell voltage than the others, attributed to the higher oxide stability of anions containing fluorine [83]. Besides, the higher capacitance of ILs associated with BF_4^- may be attributed to its smaller anionic size. In the case of $TFSI^-$, $[C_2MIm]TFSI$ was reported to have a wider electrochemical window ranging from -1.6 to 2.4 V (vs. Ag wire) [84]. The narrower cell voltage of $TFSI^-$ compared with BF_4^- in Table S2 may be attributed to the lower capacitance contributed by BF_4^- for a charge equilibrium system, which results in the decomposition of $TFSI^-$ when exceeding the electrochemical window. Owing to the higher cell voltage of 4 V, the EDLC with $[C_2MIm]BF_4$ electrolyte displays a maximum energy density of 46 W h kg^{-1} [85]. As a result, anions which are adsorbed on the positive electrodes play a key role in the charging/discharging process.

IL/organic solvent mixed electrolytes

However, within the formation of EDL, overscreening and alternating layers of counter-ions and co-ions are governed by the strong ion-ion correlations in ILs, which hamper the optimization of EDL structure [42]. On the other hand, charging of the EDLC is not only dominated by the adsorption of the counter-ions, but also dependent on the desorption of co-ions adjacent to the electrode [76]. After introducing organic solvents, the enhanced ion diffusion results in shortening the characteristic time of fast charging/discharging time, and also enhances the capacitive performance of EDLCs owing to the high dielectric constant of organic solvent that disperses ions [49]. As demonstrated in Fig. 8e, the electrochemical

performance can be improved by using appropriate ratio of IL diluted by polar organic solvents, in which 0.8 mol L^{-1} $[C_2MMIm]BF_4/AN$ mixture achieves 98% capacitance retention and 142.6 F g^{-1} of gravimetric specific capacitance, respectively [86]. On the other hand, for the EDLC with IL/organic solvent mixture electrolytes, the highest reported cell voltage is 3.5 V [7,87–89]. It is very difficult to further increase the cell voltage of this class of electrolytes. Thus, the relatively narrow electrochemical window and volatility inherent in organic solvents limit their usage in EDLCs. Meanwhile, the potential challenge for IL/organic solvent mixed electrolytes is that the solvation of ions may lower the ionic packing density and then limit the enhanced capacitance.

Functionalized ILs

It is of interest to note that the functionalized ILs, often with methylene group on the alkyl side chain of the cation replaced by an ether group, may take advantage of the merits of IL/organic solvent mixtures. An ether moiety is isoelectronic with methylene, but introduces an electro-negative center on the cation with more delocalized charge than its alkyl counterpart. Such effect reduces ion pair interactions and may also alter the EDL structure, as the ether-functionalized side chain is repelled from the cathodic polarized electrode. According to the comparison in Fig. 8f, the functionalized cation $[Pyr_{1,101}]^+$ retains higher capacitance of 206 F g^{-1} than that of the corresponding alkyl cation $[Pyr_{1,3}]^+$, which reveals that the introducing of ether bond improves the capacitance compared with the cation without ether substitution [90]. The experimental results are further confirmed by the ammonium-based IL/organic solvent mixture electrolytes, where $[N_{111(101)}]BF_4/AN$ delivers a energy density up to 13.3 W h kg^{-1} comparable to 12.7 W h kg^{-1} in $[N_{1113}]BF_4/AN$ [91]. Furthermore, the presence of functional group should be significant insight into the influence on the electrochemical window governed by both cathodic stability and anionic stability, as our key objective is to find appropriate electrolytes with wide cell voltage for high energy density of EDLCs. Despite an ether group in the cation may result in a decreased cathodic stability, which may be attributed to the reduction of the ether group at a more positive polarization potential, the ammonium-based ILs still contain wide electrochemical window, where $[Pyr_{1,101}]C_2F_5BF_3$ and $[Pyr_{1,102}]C_2F_5BF_3$ remain 5.27 and 5.22 V, respectively [92]. On the other hand, ILs with ether groups favor an increase of the fluidity and conductivity [93]. Considering the influence of functional group into ILs and ionic

Figure 9 (a) Scheme of the 3-electrode setup used for testing the voltage on the electrodes in EDLC with applied cell voltage $V = V_+ - V_-$, in which V_+ and V_- denote the voltage of anode and cathode, respectively, with respect to the reference electrode. (b) The corresponding cyclic voltammogram for the cell assembled with $[C_2MIm]TFSI$ for the entire cell (black), cathode (red), and anode (blue), with a cell voltage of 2.5 V and a scan rate 10 mV s^{-1} .

The variation of the charges on the electrode with charging or discharging time t is $Q(t) = \int_0^t I(t') dt'$. This figure clearly demonstrates the asymmetric EDLs established at the cathode and anode, though they are symmetric or identical in EDLCs. (c) Cyclic voltammograms for cells assembled with the mixture containing $[C_2MIm]TFSI$ with 20 vol% $[C_2MIm]BF_4$ at three different scan rates (20, 10, 5 mV s^{-1}). Cell voltage is 2.5 V. (d) Gravimetric specific capacitance for cells assembled with $[C_2MIm]TFSI$, $[C_2MIm]BF_4$, and 20 vol% $[C_2MIm]/BF_4$ mixtures at a constant current density of 2 A g^{-1} and applied cell voltage of 3.5 V. Reprinted with permission from Ref. [102]. Copyright 2015, Wiley.

compositions on capacitive performance, the aims are to design and optimize ILs for high capacitance and thus high energy density. Recently, oligomeric ILs with ether-bridge have been investigated as electrolyte candidates for high capacitance, while their applicability is limited at low rate process due to the higher viscosity [94–96].

IL/IL binary electrolytes

In contrast to the highest cell voltage of 4 V for $[C_2MIm]BF_4$ [85,98], the electrochemical windows of ammonium-based ILs are wider than that of the imidazolium-based ILs, as shown in Table S1. Besides, it is notable that cell voltages of EDLCs with different ILs in Table S2 are generally narrower than their individual electrochemical windows in Table S1. Therefore, utilizing the entire electrochemical windows is the significantly promising strategy to enhance the high energy density of EDLCs. For a 2-electrode assembly of EDLC in Fig. 9a,

the stored charges on anode and cathode are balanced, i. e., $Q_+ = C_+ V_+ = Q_- = C_- V_-$. Given $C_+ \neq C_-$, due to the different chemical nature of anions and cations in the formation of EDLs, a high operating potential may exceed the stability limit of electrolytes, which would lead to the decomposition of electrolytes and affect the stability of EDLCs in the whole cell voltage. Thus, the cell voltage (V) may be limited by the electrode with either lower C_+ or C_- . As described in Fig. 9b, the asymmetric shapes of cyclic voltammograms for different electrochemical stability of cations and anions, are also reflected by the asymmetric C_d in Figs 5 and 6. One strategy to enhance the balance of capacitive performance is to adjust the mass ratio between anode and cathode by $\frac{m_+}{m_-} = \frac{C_- V_{-,max}}{C_+ V_{+,max}}$ [88,89,99], in which m_+ and m_- are the masses of anode and cathode, respectively, and C_+ and C_- are the corresponding capacitance; $V_{+,max}$ and $V_{-,max}$ denote the max-

imum operating potential vs. PZC. However, such strategy can limit the gravimetric specific capacitance.

Recently, formulating IL/IL binary electrolytes was proposed to achieve balance capacitance between C_+ and C_- to increase the cell voltage and thus to enhance the energy density. The main mechanism in IL/IL mixtures is to modify the selectivity of ion adsorption by ionic electrostatic interactions and ionic steric effects (sieving effects) [100,101]. Thus, the oscillating layering structure can be optimized by increasing the overall ionic packing density and therefore decreasing the effective thickness of EDLs. In IL/IL mixed electrolytes composed by $[\text{C}_2\text{MIm}]\text{BF}_4$ and $[\text{N}_{1111}]\text{BF}_4$, the weaker interactions in $[\text{C}_2\text{MIm}]^+-\text{BF}_4^-$ may facilitate ions to enter micropores, while the cation-cation interactions between $[\text{C}_2\text{MIm}]^+$ and $[\text{N}_{1111}]$ may result in an increased packing population [100]. Van Aken *et al.* [102] altered the IL/IL mixed ratio of $[\text{C}_2\text{MIm}]\text{TFSI}$ and $[\text{C}_2\text{MIm}]\text{BF}_4$, and the mixtures with 20 vol% $[\text{C}_2\text{MIm}]\text{BF}_4$ showed the balanced potential distribution between negative and positive electrode (in Fig. 9c). In further GCD tests, $[\text{C}_2\text{MIm}]\text{TFSI}$ exhibited only 20% retention of initial capacitance with a large decay after ~4000 cycles, while the mixture with 20 vol% $[\text{C}_2\text{MIm}]\text{BF}_4$ performed the best retention of up to 95% of its initial capacitance (in Fig. 9d). The reason is that the cell voltage of 3.5 V exceeds the maximum electrochemical window for neat $[\text{C}_2\text{MIm}]\text{TFSI}$, while the addition of 20 vol% $[\text{C}_2\text{MIm}]\text{BF}_4$ enhances the capacitance C_+ contributed by anions. The enhanced capacitance originates from ionic steric volume, which balances the electrochemical window between anode and cathode. Thus, optimizing the ratio of IL composition can balance capacitance between anode and cathode, which can enhance the cell voltage and thus increase the energy storage capability of symmetric EDLCs. On the other hand, the utilization of the entire operating potential range is not only dominated by the balanced electrochemical window of anode and cathode, but also governed by the ratio of V_-/V_+ related to C_+/C_- .

Table S2 summarizes the dependence of the gravimetric specific capacitance and energy density on the compositions of IL electrolytes including pure ILs, IL/IL binary electrolytes, IL/organic solvent mixtures, as well as functionalized ILs. Understanding of experimental results in Table S2 confirms that selective of ion adsorption in the pore plays an important role in determining the electrochemical performance of EDLCs, owing to the formation of EDLs. The volumetric limitation would dominate ionic population in the pore and ionic orientation, and thus dominate the accessible surface areas,

which may affect the ionic packing density and further the thickness of EDLs. In Table S2, $[\text{C}_2\text{MIm}]\text{BF}_4$ exhibits a high energy density of 46 W h kg^{-1} with laser-scribed graphene electrode, due to its relatively high gravimetric specific capacitance of 276 F g^{-1} and relatively high cell voltage of 4 V [85]. Ionic electrostatic interactions can also drive selective ions to enter pores for high ionic density packing. The ether-functionalized IL of $[\text{Pyr}_{1,101}]\text{FSI}$, displays a high gravimetric specific capacitance of 206 F g^{-1} , partially attributed to the incorporation of ether group which provides larger accessibility of ions into the pores of the electrode surface [90]. It is notable that low cell voltage of 2.5 V for $[\text{Pyr}_{1,3}]\text{FSI}$ with a gravimetric specific capacitance of 181 F g^{-1} , limits its energy density of 11.8 W h kg^{-1} [90], which is in contrast to the wide electrochemical window of ammonium-based ILs reported in Table S1, especially 5.7 V for $[\text{N}_{1114}]\text{TFSI}$ electrolyte [16]. Thus, a balance capacitance between C_+ and C_- is essential to improve the cell voltage of ammonium-based ILs that own wider electrochemical window than the imidazolium-based ILs, further enhancing the energy density. It is also notable that IL/organic solvent mixed electrolytes do not significantly provide higher gravimetric specific capacitance compared with the pure ILs, though they exhibit higher C_d in Table S1. This apparent contradiction may be understood by noticing that C_d in Table S1 was measured with flat electrodes, while the gravimetric specific capacitances were conducted with porous electrodes. Thus, the solvation of ions in IL/organic mixed electrolytes cannot be neglected if the volumetric limitation of solvation increases the electrostatic screening length. Meanwhile, if pores were filled with organic solvents, the screening of the free charges on the electrode surface would not be as efficient as counterions.

On the other hand, most of the C_{SSA} in Table S2 is lower than the C_d in Table S1, which means that the effective SSA may not be fully utilized, and further confirms the selection of ions in pores is essential to achieve the maximal utilization of SSA with optimizing PSD. Zhang *et al.* [103] proposed estimating effective SSA (ESSA) for the accessible area via the cumulative area of the pores with size above the diameter of cations of ILs, which was generally larger than that of anions. Specifically, for $[\text{C}_2\text{MIm}]^+$ with a diameter of 0.75 nm, the ESSA is $1657 \text{ m}^2 \text{ g}^{-1}$, which is about 93% of the SSA of $1779 \text{ m}^2 \text{ g}^{-1}$. Thus, the C_{SSA} is $13.3 \mu\text{F cm}^{-2}$ using ESSA instead of $12.4 \mu\text{F cm}^{-2}$ using SSA, estimated via the gravimetric specific capacitance of 220 F g^{-1} . This report provides a nice attempt to estimate the upper limit of

ESSA. The highest C_{SSA} from Table S2 is $24.9 \mu\text{F cm}^{-2}$, using a small size IL, $[\text{C}_2\text{MIm}]\text{BF}_4$, with graphene sheet electrodes with dominant average pore size about 3.6 nm [83]. Thus, such high C_{SSA} may be understood as 100% usage of SSA of $481.5 \text{ m}^2 \text{ g}^{-1}$, with additional gain *via* the nano-confined ions [70]. Unfortunately, the relatively smaller SSA gives a gravimetric specific capacitance of 120 F g^{-1} . Therefore, a large ESSA is essential to high gravimetric specific capacitance as well as the appropriate PSD, owing to the large area accessibility and the favorability of the ionic orientation in the pores.

At this point, it is of interest to estimate the upper limit of EDLCs. It was reported the quantum limit of a perfect graphene C_{SSA} is $21 \mu\text{F cm}^{-2}$ [104]. Considering the theoretical SSA of perfect graphene of $A=2630 \text{ m}^2 \text{ g}^{-1}$ [87,105], the theoretical gravimetric specific capacitance of graphene is $\sim 550 \text{ F g}^{-1}$ [85]. In addition, if SSA of $2630 \text{ m}^2 \text{ g}^{-1}$ is available by 80% for charging/discharging process, the above theoretical capacitance can decay to $\sim 440 \text{ F g}^{-1}$ [106]. Assuming further that the electrode materials take 30% of the total weight of a symmetric EDLC with a cell voltage of 4.0 V, the energy density of such assembled EDLC would be 73 W h kg^{-1} . Would this be the upper limit of EDLC? Not necessary! Based on the above studies, (1) the introduction of ILs as electrolytes can greatly enhance the electrochemical window up to 5 V; (2) the recently reported defective graphene has larger SSA up to $3523 \text{ m}^2 \text{ g}^{-1}$ [79]; (3) nano-confined IL pore can deliver high capacitance [70]. Thus, there is still much room to improve the energy density of IL-based EDLCs.

IL GEL POLYMER ELECTROLYTE INSTEAD OF LIQUID ELECTROLYTE APPLIED IN EDLC

Considering the electrolyte leakage problem, IL gel polymer electrolytes (IL-GPEs) are applied in solid-state EDLCs instead of liquid electrolytes. Normally, IL-GPEs possess high ionic conductivity and flexibility as well as wide operating voltage and nonflammability, almost comparable to liquid electrolytes [107]. These advantages help to develop flexible structures and tunable shapes for various applications [2]. Generally, GPEs essentially consist of host polymer matrix, transport electrolyte ions and plasticizers [108]. In IL-GPEs, ILs are assumed as both transport electrolyte ions and plasticizers. A schematic illustration of IL-GPEs as a media to transport ions and separator between two electrodes in a solid-state EDLC is described in Fig. 10a. The charging and discharging mechanisms in EDLCs confirm the fact that

Figure 10 (a) Scheme of solid-state EDLC with IL-GPEs. Reprinted with permission from Ref. [116]. Copyright 2016, Elsevier. (b) The cyclic stability of IL-GPEs with increased cationic size at a current density of 1.0 mA cm^{-2} . Reprinted with permission from Ref. [108]. Copyright 2018, Elsevier. (c) Cycling performance of $[\text{Pyr}_{1,3}]\text{TFSI}$ -GPEs on AC electrode and MWCNT added AC electrode. Reprinted with permission from Ref. [111]. Copyright 2018, Elsevier.

charge storage predominantly involves surface diffusion ($<10 \text{ nm}$), and is not controlled by bulk diffusion of ions across the cell [46,109]. However, it should be noted that the limited contact surface area between IL-GPEs and electrode materials, could increase the internal resistance and limit the utilized SSA of electrodes [2]. To date, various polymer matrices have been used in solid-state EDLCs, including poly(vinylidene fluoride) (PVdF), poly(hexafluoropylene) (PHFP), poly(vinylidene fluoride-co-hexafluoropylene) (P(VdF-HFP)), poly(methyl methacrylate-co-dopamine methacrylate) (P(MMA-DMA)), and etc. [110]. Among them, P(VdF-HFP) copolymer is mostly utilized to prepare IL-GPEs owing to the semi-crystalline structure containing both crystalline and amorphous behaviors [111], while standard solution cast technique is frequently used in preparation of IL-GELs [112,113].

As reported, a solid-state EDLC with IL-GPEs can achieve higher capacitive performance than that using liquid electrolytes [114,115]. Pandey *et al.* [116] found that with the incorporation of $[\text{C}_4\text{MIm}]\text{BF}_4$ -GPEs, the solid-state EDLCs showed a specific capacitance of 110 F g^{-1} , which was higher than 77 F g^{-1} for that with $[\text{C}_4\text{MIm}]\text{BF}_4$ -liquid electrolytes. Interestingly, the properties of ILs and the SSA of electrode materials also play

an important role in the performance of solid-state EDLCs. In Fig. 10b, a comparison of capacitive performance of IL-GPEs with different cationic sizes demonstrates that the gravimetric specific capacitance increases with the decreased cationic size, where a high specific capacitance of 113.6 F g^{-1} is obtained at 1.0 mA cm^{-2} with smaller size of $[\text{C}_2\text{MIm}]^+$ [108]. As described in Fig. 10c, the electrode properties influence the cyclic stability of $[\text{Pyr}_{1,3}]\text{TFSI}$ -GPEs-based solid-state EDLCs, where a higher specific capacity retention of 75% is obtained by multi-wall carbon nanotube (MWCNT) added AC (MWCNT-AC) electrode compared with 48% for the AC electrode [111]. The results are very consistent with the capacitive performance in EDLCs with liquid electrolytes, where volumetric limitation of ions dominates the formation of EDLs. Therefore, fundamental understanding of liquid electrolytes in EDLCs is helpful to prepare IL-GPEs incorporated with electrodes, which can also benefit IL-GPEs as promising candidates for the development of solid-state EDLCs.

Recently, some efforts were devoted to achieving high performance of solid-state EDLCs. Zhang *et al.* [117] prepared the supported IL-gel membrane electrolytes (IL-GMEs) by incorporating IL-gel into commercial porous supports. They found that the solid-state EDLCs with $[\text{C}_2\text{MIm}]\text{TFSI}$ -GMEs exhibited a high gravimetric specific capacitance of 153 F g^{-1} and excellent cycle stability, with as high as 97% of the original capacitance after 10,000 charging/discharging cycles. Yang *et al.* [114] reported that the addition of conductive graphene oxide (GO) could significantly improve the conductivity of IL-GPEs. The solid-state EDLCs with GO-doped $[\text{C}_2\text{MIm}]\text{BF}_4$ -GPEs exhibit better cycle stability and a high specific energy density of 9.7 W h kg^{-1} . Jin *et al.* [118] prepared a high-performance boron-containing GPE with semi-interpenetrating polymer network structure incorporating with the anion-trapping boron sites, which was beneficial to a better capacitance retention of 91.2%. One of the recent host polymers is the poly(ionic liquid) (PIL) by polymerizing the IL itself [119–121]. de Oliveira *et al.* [122] investigated the influence of the synthesized PIL/IL-GPEs on the properties of solid-state EDLCs. They found that the solid-state EDLCs with binary blend of poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PILTFSI) and $[\text{C}_3\text{MMIm}]\text{TFSI}$ -GPEs maintained 93% of capacitance after 1000 cycles, which was remarkably higher than that of solid-state EDLCs with $[\text{C}_4\text{MIm}]\text{FSI}$ -GPEs. The results demonstrate that the match of the properties of ILs with the PIL's is important in the charge storage of solid-state

EDLCs.

SUMMARY

EDLCs store free charges on the electrode surface *via* non-Faradaic process, which is balanced by the EDL formed by the counter-ions in the electrolytes. Thus, EDLCs exhibit high cycle stability and excellent power density. Owing to their environmental benignity and wide electrochemical windows (up to 5 V), ILs are considered as promising electrolytes in EDLCs with high energy density. In this review, we focus on the ILs that are potentially capable of fulfilling such goal, and also focus on both the C_d with flat electrode to explore the EDL structures with small effective EDL thickness, as well as the gravimetric specific capacitance with porous carbon materials electrode with high SSA and appropriate PSD. The chemical composition of ILs, ionic sizes, ionic structures and ionic interactions play key roles in the formation of EDL, along with the SSA and PSD of electrode materials.

Imidazolium- and ammonium-based ILs are the most widely investigated electrolytes in EDLCs. The experimental results demonstrate that the volumetric limitation dominates the ionic packing density in the pore, owing to the sieving effect and ionic orientation, which may be also governed by the ionic interactions and interactions between ions and electrodes. For pure ILs, $[\text{C}_2\text{MIm}]\text{BF}_4$ can exhibit a high gravimetric specific capacitance of 276 F g^{-1} [85], while $[\text{Pyr}_{1,3}]\text{FSI}$ displays a gravimetric specific capacitance of 181 F g^{-1} [90]. Thus, a high energy density can be up to 46 W h kg^{-1} for $[\text{C}_2\text{MIm}]\text{BF}_4$ with a cell voltage of 4 V [85]. The charging EDLs formed on the electrode surface with oscillation layering and overscreening originated from strong ionic interactions of ILs, would limit the capacitive performance of EDLCs. Considering such overscreening effect in EDLs, ILs diluted with organic solvents and functionalized by organic group are proposed as efficient strategies. When organic solvents disperse ions, $1.0 \text{ mol L}^{-1} [\text{N}_{2222}]\text{BF}_4/\text{AN}$ mixture achieves 202 F g^{-1} for gravimetric specific capacitance [79]. It is also notable that IL/organic solvent mixtures, though generally have higher capacitance than the pure ILs, do not deliver higher energy density in EDLCs compared with the pure ones. The reason may be attributed to the pores filled with the organic solvent, which results in inefficient screening of the electrode charge as well as the narrow electrochemical window of the organic solvent. Functionalized IL with electronegative group on the cations, such as $[\text{Pyr}_{1,10}]\text{FSI}$ with ether-substituent exhibits a higher gravimetric specific capacitance of

206 F g⁻¹ than that of 181 F g⁻¹ for [Pyr_{1,3}]FSI [90]. It is notable that the influence of the solvation of ions on the formation of EDLs and the organic group/organic solvents on the electrochemical window cannot be neglected.

On the other hand, a high energy density can be up to 46 W h kg⁻¹ for [C₂MIm]BF₄ with a cell voltage of 4 V [85]. Generally, the ammonium-based ILs have wider electrochemical window compared with imidazolium-based ILs according to the measurements in three electrode system. However, the entire electrochemical window of most ILs may not be fully utilized in two-electrode EDLCs, due to unbalance of capacitance between anode and cathode, which results in limitation of cell voltage by the decomposition of electrolyte ions. The balance of capacitance between cathode and anode is essential to impose high cell voltage for ammonium-based ILs, which can further optimize the cycle stability and energy density.

Based on the current studies of IL electrolytes in EDLCs, it can be found that the smaller ions can penetrate into pores and thus may contribute to higher energy density than bulky ions. On the other hand, the strong ionic correlation correlated with small ions, and ion pairs do not contribute to the EDL capacitance, or their contributions are limited if considered as dielectrics. This results in the insufficient screening of the electrode potential, further depresses the capacitive performance and affects the specific energy. In order to overcome the drawback of neat ILs, functionalized ILs with electro-negative group on the cations may inherent the higher capacitance as IL/organic solvent mixtures, while keeping a wide electrochemical window. The cell voltage of EDLCs may be optimized with IL/IL mixtures. Additionally, fundamental understanding of capacitive performance in liquid electrolytes of ILs is useful to design “designer transport ions” and to prepare electrodes incorporated with IL-GPEs, which can also benefit IL-GPEs as promising candidates for the development of solid-state EDLCs. Based on the above consideration, it is worthy to further explore the ammonium-based ILs with wide electrochemical window, mixing with functionalized ILs to increase capacitance with balanced cell voltage, in the practical applications of EDLCs toward higher energy density.

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离子液体电解液在双电层电容器中的研究

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摘要 双电层电容器(EDLCs)通过非法拉第过程在电极表面储存自由电荷, 其通过电解质侧的双电层平衡, 具有优异的循环稳定性和高功率密度。虽然EDLC被认为是具有前景的能量储存器件, 但其电极表面存储的电荷远低于电池, 其较低的能量密度限制了其应用。离子液体(ILs), 因其较宽的电化学窗口和独特的物理化学性能, 可显著提高EDLCs的能量密度。本文综述了纯ILs、IL/IL二元混合体系、IL/有机溶剂混合体系以及功能化ILs等电解液, 着重探讨了ILs的离子组成、尺寸、结构与电容的关系。咪唑类和季铵盐类ILs作为目前研究最广泛的两类ILs, 前者一般具有较高的重量比电容, 后者则表现出更宽的电化学窗口。故可对季铵盐类ILs进行官能化以提高其重量比电容, 进而提高EDLCs的能量密度。