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Review

Tuning of Ionic Liquid–Solvent Electrolytes for High-Voltage Electrochemical Double Layer Capacitors: A Review

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Abstract: Electrochemical double-layer capacitors (EDLCs) possess extremely high-power density and a long cycle lifespan, but they have been long constrained by a low energy density. Since the electrochemical stability of electrolytes is essential to the operating voltage of EDLCs, and thus to their energy density, the tuning of electrolyte components towards a high-voltage window has been a research focus for a long time. Organic electrolytes based on ionic liquids (ILs) are recognized as the most commercially promising owing to their moderate operating voltage and excellent conductivity. Despite impressive progress, the working voltage of IL–solvent electrolytes needs to be improved to meet the growing demand. In this review, the recent progress in the tuning of IL- based organic electrolyte components for higher-voltage EDLCs is comprehensively summarized and the advantages and limitations of these innovative components are outlined. Furthermore, future trends of IL–solvent electrolytes in this field are highlighted.

Keywords: EDLCs; electrolytes; IL–solvent; high-voltage; component tuning

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Citation: Wang, Y.; Xue, K.; Yan, C.; Li, Y.; Zhang, X.; Su, K.; Ma, P.; Wan, S.; Lang, J. Tuning of Ionic Liquid–Solvent Electrolytes for High-Voltage Electrochemical Double Layer Capacitors: A Review. *Batteries* **2024**, *10*, 54. https://doi.org/10.3390/batteries10020054

Academic Editor: Douglas Ivey

Received: 12 December 2023
Revised: 22 January 2024
Accepted: 25 January 2024
Published: 2 February 2024

1. Introduction

Renewable forms of energy, including solar, wind, hydroelectric, geothermal, and biomass, are essential to move forward the sustainable economy [1]. However, these renewable energies have the disadvantages of intermittency and require the participation of energy storage devices [2]. Reversible energy storage and discharge technology has become indispensable, requiring the development of systems that deliver both high energy and high-power capability. Electrical energy can be stored electrochemically in batteries and capacitors. Various types of batteries include lithium-ion batteries (Li-ion), sodium–sulfur batteries (Na–S), lead–acid (Pb–acid) batteries, and flow batteries. Among the various types of battery systems, lithium-ion batteries hold the dominant position in the market with their energy density of up to 300 Wh/kg. Nevertheless, their power density and lifetime are constrained by the mechanism of store charge, that is, the change is converted into electrical energy through an electrochemical redox reaction. Moreover, the batteries always face the problem of short life and slow charging rate due to the limitations of volume charge, phase transition, and solid diffusion rate during charging and discharging.

Electrochemical double-layer capacitors (EDLCs) [3,4], also referred to as supercapacitors, store and release energy based on charge adsorption and desorption on electrode surfaces (Figure 1b). Therefore, they exhibit advantages such as exceedingly high power

density (>10 kW kg^{-1}), rapid charging/discharging, and an extremely long cycle life. The devices do not undergo Faraday reactions during operation, making their charge and discharge processes very effective, and the cycle life significantly surpasses other energy storage devices. Thus, EDLCs are considered as a promising renewable energy storage device and have become the preferred technology for applications that need to provide a rapid and sustained energy supply [5]. Moreover, EDLCs are suitable for incorporation into grid energy storage to conserve power units and for frequency regulation, as well as to enhance power quality and smoothness. As a result of the application of these features, the global EDLC market continues to grow, which can be observed in Figure 1c. Among the regional markets, the Asia–Pacific region has great potential for market growth in the upcoming years, whereas Europe and North America also hold a considerable market share.

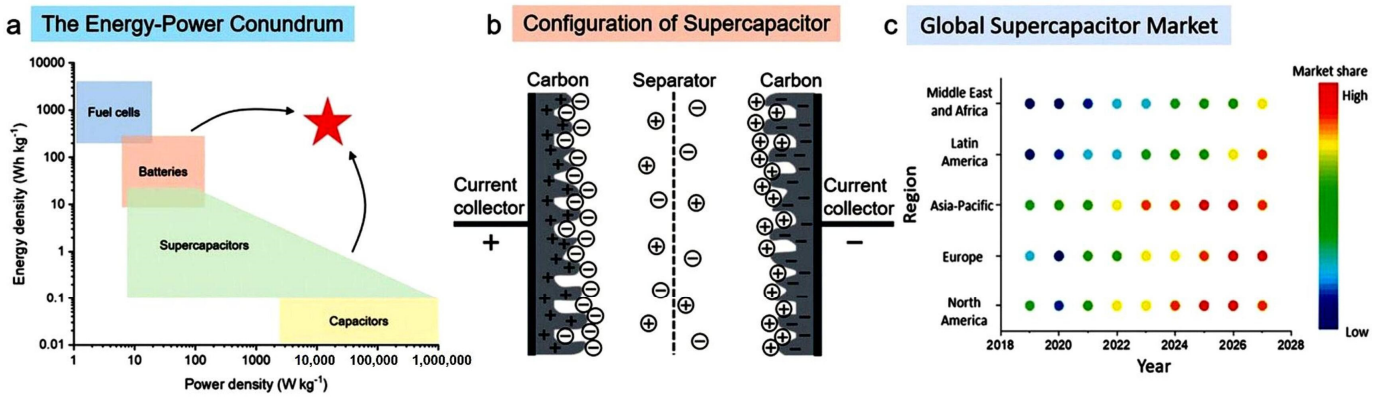

Figure 1. (**a**) A Ragone plot depicting various energy storage systems; (**b**) fundamental design and operational principles of an EDLC; (**c**) global distribution of supercapacitor market shares by region and year [3].

Typically, the energy density of an EDLC is determined by its electrodes and electrolytes [6]. Based on the equation of energy density ($E = 1/2\ CV^2$, where C is the capacitance of the electrodes and V represents the operating voltage window) [7], one strategy is to develop novel electrode materials to deliver higher capacitance. Carbon-based materials have become the most widely studied active materials [8,9] due to their excellent chemical and thermal stability. According to the basic structure and shape of carbon materials, three main types of carbon-based materials for symmetrical EDLCs are as follows: (I) graphene [10,11] and carbon nanotubes [12,13]; (II) carbide-derived carbon and aerogels [14,15]; and (III) activated carbon (AC) [16,17]. Nevertheless, the reported specific capacitance for alternative materials typically ranges between 100 and 150 F g^{-1}, which is not significantly superior to activated-carbon-based electrodes. Strategies for modifying carbon-based materials have been employed in high-voltage EDLCs, encompassing methods like heteroatom doping, selection of diverse raw precursor materials, activation techniques for AC, and controlling the growth process of CNT to prevent the formation of amorphous carbon. However, the synthesis process of these carbon materials for high-voltage uses is considered to be complex and costly, which is not suitable for industrial application. Apart from increasing the specific capacitance of electrodes [18], expanding the operating voltage window (V) is another efficient technique for enhancing the energy density. Meanwhile, the operating voltage of EDLCs is closely associated with the properties of the electrolyte, which are mainly limited by the electrochemical stability of the electrolyte. Due to this consideration, the development of alternative electrolyte salts, or the tuning of electrolyte composition, represents one of the keys to achieving high-energy EDLCs nowadays [19–21].

Ionic liquids (ILs) are salt-like materials formed by ionic bonds between cations and anions. Due to their wide electrochemical potential windows, high thermal and chemical stability, non-volatility, and non-combustibility, ILs can significantly help EDLCs obtain

higher energy densities than aqueous electrolytes. Therefore, ILs as electrolytes in EDLCs have garnered considerable interest [22]. To date, extensive research has been conducted on IL-based electrolytes, including pure ILs, binary mixtures of ILs, and ILs combined with organic solvent electrolytes. Among them, solvent-free IL–electrolytes can provide the highest operating voltage window in the range of 3–4 V for the carbon–electrode combination [23]. However, due to large ion sizes, their high viscosity and low ionic conductivity limit the dynamic behaviors of the EDLCs by ionic diffusion. Moreover, the high cost of neat ILs also poses a challenge for the commercialization of EDLCs. IL–organic solvent electrolytes, featuring a moderate operating voltage window, are the most extensively commercialized type of electrolyte for EDLCs at present. However, the operating voltage of EDLC devices using commercial tetra–ethylamine tetrafluoroborate ($TEABF_4$)/acetonitrile electrolyte is limited to 2.8 V. Thus, the development of a novel IL-based electrolyte with a voltage up to 3.0 V or higher has been a research hotspot in this field.

Recently, many studies have focused on developing suitable IL–solvent electrolyte components for EDLCs to attain increased voltage and enhanced energy density. IL–solvent electrolytes were mentioned in some reviews [21,24,25] as the key materials of high-energy-density EDLCs, but so far, no review has summarized in great detail the tuning of the components of IL–solvent for the high voltage requirement. Therefore, this review will focus on the tuning strategies for high-voltage IL–solvent electrolytes for EDLCs that have been executed so far, focusing on the tuning of concentration, solvent composition, and the solute salt component of electrolytes based on common ILs, as well as the design principle. At the same time, we also hope to provide reference strategies for the further development of advanced electrolytes in the future.

2. Electrolytes for EDLCs

Electrolytes are the important components of EDLCs, affecting the electrochemical performance, operation life, and safety. Electrolytes with high voltage and ionic conductivity have demonstrated a substantial enhancement in the overall performance of energy storage devices [26]. The cell voltage is mainly limited by the electrochemical stability window (ESW) of the electrolyte, which is defined as the range between the reduction potential and oxidation potential. The ESW is influenced by the characteristics of ions and solvents, along with the interactions between ion–ion, ion–solvent, and electrode–electrolyte surfaces. Several studies have suggested that the decomposition of the electrolyte can be attributed to the presence of catalytic active centers, particularly functional groups on the carbon electrode [27].

Electrolytes primarily consist of solute salts and solvents, in which the solute salts provide ions and the solvents facilitate pathways for the transport of these electrolyte ions. The electrolytes can be classified into liquid electrolytes and solid electrolytes [28,29], and the liquid electrolytes can be further classified into aqueous electrolytes and non-aqueous electrolytes according to the types of solvents. The liquid electrolytes used in EDLCs include aqueous and organic electrolytes and pure ILs (Table 1). Aqueous electrolytes possess inherent advantages, including safety, low cost, high conductivity (~1 S cm^{-1}), minimum ion-pairing possibility, and environmental friendliness [30]. The ionic conductivity of aqueous electrolytes significantly surpasses that of non-aqueous electrolytes, resulting in superior rate performance. Nevertheless, the stable window of water is limited to only 1.23 V, which imposes constraints on the practical application of aqueous electrolyte [31–33]. "Water–in–salt" (WIS) electrolyte refers to an electrolyte with an exceptionally high concentration that approaches saturation levels. The number of "free" water molecules is lower than that of the solute molecules, so WIS electrolytes can increase the operating voltage of aqueous EDLCs [34–37]. Until now, the working potential voltages of symmetric EDLCs assembled by AC electrode and WIS electrolyte are still $\leq$3.0 V [38]. In contrast, organic electrolytes [39,40] have wider stable electrochemical potential windows of 2.5–3.0 V and therefore are more preferred than aqueous electrolytes.

Table 1. Electrolytes used in EDLCs.

Types	Electrolytes	Operating Voltage (V)	References
Aqueous electrolyte	6M KOH,6M NaOH, 1M HCl, 0.5M H_2SO_4	0.9	[33]
	1M NaCl, 1M KCl, 0.5M Na_2SO_4, 0.5M K_2SO_4	1.7	[34]
	0.5M H_2SO_4	1.2	[34]
	LiCl (1M, 10M, 20M)	1.4, 1.5, 2.35	[34]
	KCH_3COO	2.0	[38]
	WIS (21M LiTFSI)	2.2	[35]
	WIS (21M LiTFSI)	2.6	[36]
	WIS (31.3M LiTFSI)	2.4	[37]
Solvent-free ILs	$EMImBF_4$	3.5	[41]
	EMImFSI	2.0	[42]
	EMImTFSI	3.0	[43]
	$Pyr_{14}TFSI$	3.7	[44]
	MPImFSI	3.5	[45]
	MPPyrFSI	3.5	[45]
	MeoMPyrFSI	3.5	[45]
	$Pip_{14}B(CN)4$	3.7	[46]
	$Pyr_{14}B(CN)4$	3.7	[46]
Mixed ILs	EMImTFSI + $EMImBF_4$	3.5	[47]
	$Pyr_{14}FSI$ + $PIP_{13}FSI$	3.7	[48]
	$EMImBF_4$ + $TMABF_4$	3.5	[41]
	EMImTFSI + MPPyrTFSI	3.5	[49]
IL–solvent	$Pyr_{14}TFSI/AN$	3.1	[50]
	$Pyr_{14}BF_4/AN$	3.1	[50]
	$Pyr_{14}BF_4/PC$	3.2	[51]
	$TEABF_4$/AN or PC	2.5–2.8	[52]
	$SBPBF_4$/AN or PC	2.8–3.2	[53]
	($TEMABF_4$; $DEDMABF_4$; $TMPABF_4$; $TMEABF_4$)/AN	3.0	[54]

ILs are unique ionic compounds composed of organic cations and organic/inorganic anions. They are also described as molten salts with melting points below 100 °C [55]. ILs are also known for their remarkable properties, including the ability to maintain liquid state over a wide temperature range, negligible vapor pressure, and high thermal stability. The higher electrochemical stability and thermal stability of ILs make them well-suited for high voltage and high-temperature supercapacitors. The cations of ILs can be classified as imidazolium [42,43], pyrrolidinium [44,45], pyridinium, piperidium, quaternary ammonium [54], and quaternary phosphonium. So far, ILs utilizing pyrrolidinium, ammonium, and imidazolium cations are the most promising and widely utilized types. In general, the pyrrolidinium-based ILs have higher electrochemical stability than imidazole-based ILs, while the imidazole-based ILs show higher conductivity and lower viscosity than pyrrolidinium-based ILs [56]. These features make pyrrolidinium-based ILs suitable for greater energy output, while imidazole-based ILs have fast charge/discharge performance. The conventional ILs in EDLCs are based on cations of 1–ethyl–3–methylimidazolium (EMIm) [41], N-propyl-N-methylpyrrolidinium (Pyr_{13}), 1–butyl–1–methylpyrrolidinium (Pyr_{14}) [50], 1–butyl–3–methylimidazolium (BMIm) [57]. Additionally, the most commonly used anions include bis(trifluoromethanesulfonyl)imide ($TFSI^-$), hexafluorophosphate (PF_6^-), bis(fluorosulfonyl)imide (FSI^-), and tetrafluoroborate (BF_4^-). These reported ILs exhibited operating potential windows up to 3.5 V or ever higher when used alone as electrolytes [58]. Furthermore, the structure of the most commonly used anions and cations for ILs is depicted in Figure 2a [59]. In addition, some new ILs (Figure 2b), such as azepanium [60], acetate- and lactate-based piperidinium [46], piperazinium [61], and bis(oxalate)borate-based ILs [62] have been reported for EDLCs (Figure 2b). Relevant reviews have summarized the regulation of the cation and anion structures of ILs used in EDLCs [63,64]. The adjusting methods of the structures include the optimization of side

chain lengths for cations and incorporation of functional groups into the cations, such as substituting F with the electron-withdrawing substituent (–CN). Mixed ILs with different anions or cations could alter the initial ion accumulation due to the difference in ion sizes, thereby adjusting the thickness of the electric double layer on the electrode interface and the distribution of ions within the nanopores, which lead to the excellent electrochemical performances of EDLCs, such as wide operating voltage, high capacitance, and long cycle life [41,47–49]. However, solvent–free single ILs and mixed ILs are not utilized in commercial devices owing to their drawbacks such as high expense, limited transport properties, and excessive viscosity. Therefore, the reasonable selection and manipulation of IL-based electrolytes to exploit their advantages and solve their shortcomings will be the future direction of building EDLCs with high energy density.

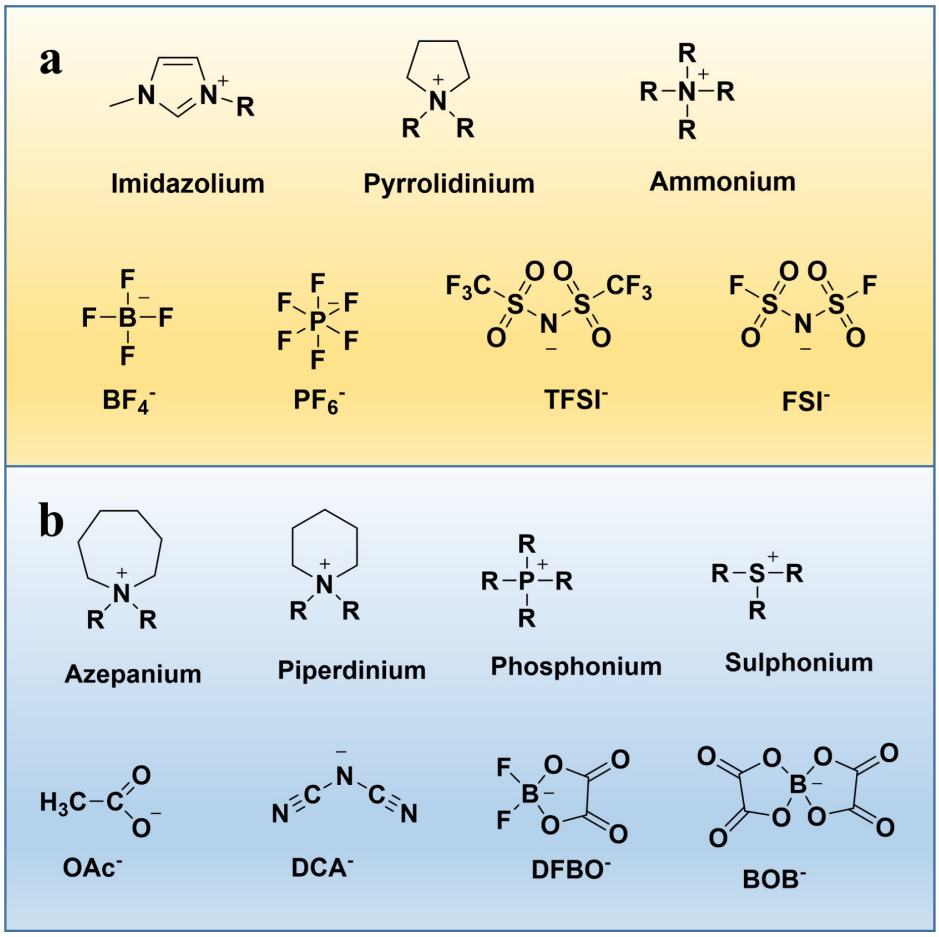

Figure 2. Commonly used cations and anions (**a**) and other cations and anions with new structure (**b**) in ILs.

The cations and anions in ILs are bound by potent Coulombic forces and van der Waals forces, resulting in the high viscosity, low conductivity, and low ion migration rate of ILs. Thus, adding organic solvents to ILs would weaken the Coulombic force and van der Waals force to alleviate the drawbacks of low conductivity and high viscosity of pure ILs. In IL–solvent electrolyte, ILs provide a similar role to other salts, supplying cations and anions in organic solutions. The operating voltage windows of EDLCs with these IL–solvent electrolytes are 2.7–3.0 V [65], which are generally lower than that of pure-IL electrolytes (Table 1). Therefore, EDLCs using IL–solvent electrolytes have moderate operating voltage windows between aqueous electrolytes and pure-IL electrolytes and have excellent electrical conductivity; thus, they are the most widely commercialized currently. The majority of commercially available organic electrolytes are solutions of 1 M

ammonium salt, often $TEABF_4$, dissolved in organic solvents like propylene carbonate (PC) or acetonitrile (AN) [66]; their operating voltages are 2.7–2.8 V. Compared with PC-based electrolytes, AN-based IL electrolytes are more commonly used due to their higher conductivity and superior performance at low temperatures. However, the voltage window of the IL–solvent electrolyte system still has a lot of room for improvement. Therefore, increasing the operating voltage of EDLCs using IL–solvent electrolytes is still the research direction in this field, and it is also the focus of this review. There have been some reviews on the structure regulations of ILs and their application in EDLCs [67–71], so many reports on the use of innovative pure ILs as electrolytes for EDLCs are out of the scope of this article.

3. Tuning of IL–Solvent Electrolytes for EDLCs

At high operating voltage, the electrolyte components may decompose on the surface of the carbon-based active material, resulting in an irreversible electrochemical process for the device [72,73]. Therefore, the stability of each component of the electrolyte determines the operating voltage limit. Over recent years, many efforts have been made to develop advanced IL–solvent electrolyte systems to meet the necessary criteria for achieving high-energy EDLCs. At present, for the existing IL solute salts, the methods of tuning IL–solvent electrolyte components to achieve higher voltage can be divided into four categories (Figure 3): (1) increasing the concentration of IL solute salts; (2) selecting single-substitute solvents with high electrochemical stability to replace AN and PC; (3) adding co-solvent to AN or PC to improve the electrochemical stability or conductivity; and (4) introducing solute salt additives.

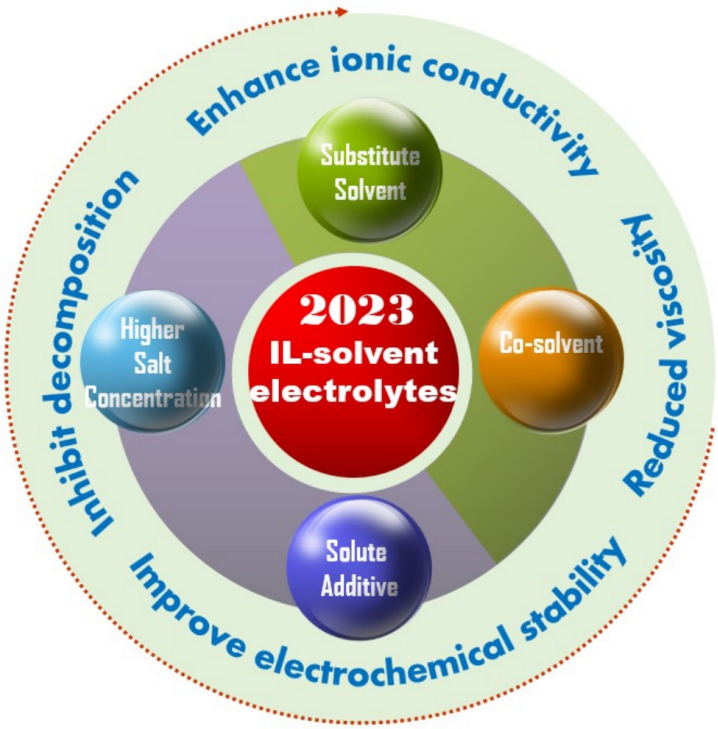

Figure 3. The methods of increasing the voltage of IL–solvent electrolytes as well as the corresponding improved physicochemical properties.

3.1. Higher Salt Concentration for High Voltage

The concentration of solute salt in commercial electrolyte is usually 1.0 M. The energy density of EDLCs is determined by the quantity of electrolyte ions per unit area of the electrode surface. The IL concentration plays a pivotal role in regulating viscosity, ionic liquid conductivity, and the potential window. Higher salt concentration can not only increase the number of adsorbed/desorbed ions, which may increase the specific capacity (C), but also has been considered as a method to break through the voltage limits of EDLCs [74],

because less free solvent molecules will reduce the redox reaction on the electrode. For example, the use of 2.0 M N,N–dimethyl pyrrolidinium tetrafluoroborate ($Pyr_{11}BF_4$)/AN [75], enabled the EDLC to achieve a high operating voltage of 3.4 V with a capacitance retention of 88% after 500 h. In addition, EDLCs using higher-salt-concentration electrolytes also surpassed the current leading devices in terms of high-temperature performance (retaining 91% capacitance after floating 500 times at 3.0 V and 60 °C) (Figure 4a,b). Meanwhile, post-mortem gas chromatography/mass spectrometry (GC–MS) indicated that the higher performances of 2M $Pyr_{11}BF_4$/AN were related to its high thermal and electrochemical stability. In addition, a Pyr_{14}TFSI/PC (1:1 wt.%) mixture (equivalent to a concentration of 2.3 M) [51] provided the operating voltage of the EDLCs at 3.5 V, which was similar to that of EDLCs using neat Pyr_{14}TFSI. The electrolyte system also ensured excellent cycle stability, with a 5% decrease in capacitance after 100,000 cycles at 3.5 V. Another report of 2.3 M $Pyr_{14}BF_4$/PC electrolyte [76] indicated that the electrolyte allowed the cells to work at a high operating voltage of 3.2 V in a float test, and the conductivity and viscosity were comparable to those of the traditional 1.0 M Et_4NBF_4/PC electrolyte. Moreover, due to the high electrochemical stability of electrolyte, the high cycle stability of EDLCs at 3.2 V was confirmed by charge-discharge measurement. $EMImBF_4$ with small contents (from 0.005 M to 1.0 M) of different organic solvents (AN, PC or γ–butyrolactone) [77] were studied as electrolytes in EDLCs at high potentials (≥3.2 V). Jia et al. [52] systematically studied the effect of $EMImBF_4$ concentrations (including 1.0 M, 2.0 M, 4.0 M, and 6.54 M) on the potential window, ionic conductivity, and viscosity of the $EMImBF_4$/AN electrolyte. The results show that the ESWs of FRGO-based EDLCs increased with increasing IL concentrations: 1M $EMImBF_4$/AN (3.4 V), 2M $EMImBF_4$/AN (3.4 V), and 4M $EMImBF_4$/AN (3.5 V). The increase in specific capacitances had a similar trend: 1M $EMImBF_4$/AN (94.4 F g^{-1}), 2M $EMImBF_4$/AN (147.8 F g^{-1}), and 4M $EMImBF_4$/AN (158.3 F g^{-1}). The maximum specific capacitance offered by the 4M $EMImBF_4$/AN was due to the fact that the capacitance of EDLCs increased with the increase in voltage across electrodes. The reason for the low ESW of dilute solution was that the "freer" AN molecule was prone to irreversible redox reactions on the electrode surface. With rising IL concentrations, the viscosity of the electrolytes increased, whereas the ionic conductivity decreased. The peak was reached when the concentration of $EMImBF_4$ was 2.0 M (Figure 4c–f).

Scalia et al. [78] used N–butyl–N–methyl–pyrrolidinium 4,5-dicyano-2–(trifluoromethyl) imidazole (Pyr_{14}TDI) as the solute salt for EDLCs for the first time and evaluated the performances of the electrolytes with different Pyr_{14}TDI/PC ratios from 1:3 to 3:1 (w/w). By adjusting the concentrations of the solution, a wide liquid range and high conductivities were achieved. The highest cell voltage of 3.3 V was attained with a Pyr_{14}TDI/PC ratio of 3:1. Meanwhile, although the voltage window of the most diluted electrolyte Pyr_{14}TDI:PC (1:3) was limited to 3.0 V, it delivered the highest specific energy and power. Balducci et al. [79] explored the impact of salt concentrations on the theoretical and practical energy of EDLCs with PC-based $Pyr_{14}BF_4$ and trimethylsulfonium bis[(trifluoromethyl)sulfonyl]imide (Me_3TFSI). The study indicates that 1.5 M $Pyr_{14}BF_4$/PC and 3.8 M Me_3TFSI/PC were promising for higher operative voltages of 3.49 V and 2.88 V, respectively.

Based on the examples given above, a high concentration of IL–solvent electrolyte does have a significant effect on raising the voltage, but the reasons for the formation of this electrochemical stability in high-concentration electrolytes have not been clearly studied. Moreover, there are still some shortcomings to limit their commercial application, such as low conductivity, high viscosity, and high cost.

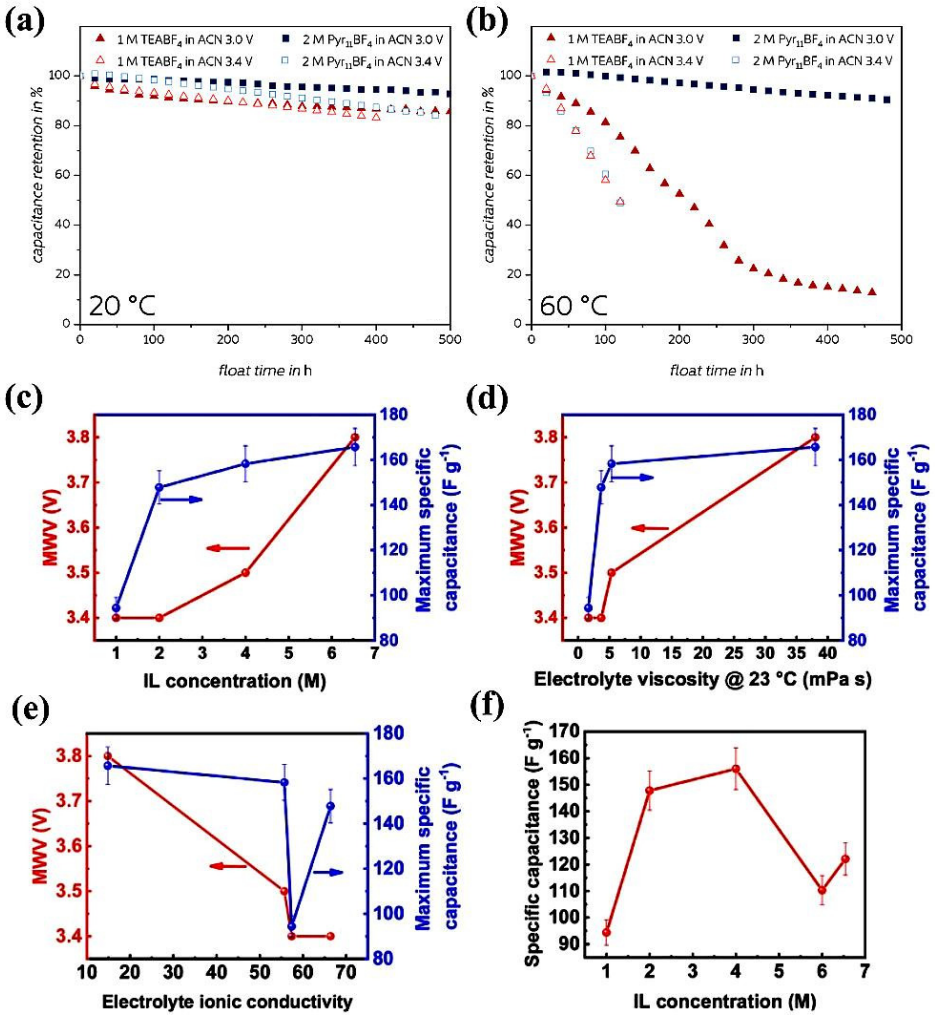

Figure 4. Comparisons of the floating stability of 1 M $TEABF_4$/AN and 2 M $Pyr_{11}BF_4$/AN at 20 °C (**a**) and 60 °C (**b**) [75]. The maximum operating voltages (MWVs) and maximum specific capacitance related to (**c**) the concentration of IL, (**d**) the viscosity of the electrolyte, and (**e**) the ionic conductivity of electrolytes. The variation curve of specific capacitance with IL concentration at 3.4 V (**f**) [52].

3.2. The Use of Single-Substitute Solvent with High Electrochemical Stability

AN and PC are the commonly used organic solvents in the electrolyte for EDLCs. With regard to improving the stable voltage window of IL-based electrolytes, several organic solvents with higher electrochemical stability were proposed and tested as the alternative solvents of AN and PC [80], such as ethyl isopropyl sulfone, propionitrile, adiponitrile, and butylene carbonate. Ethyl isopropyl sulfone (EiPS) has a high boiling point (265 °C) and a relatively low melting point (−8 °C) and low reactivity with water, which makes it a potential organic solvent for high-voltage EDLCs [81,82]. Balducci et al. [83] further studied the electrochemical performance of EDLCs using $TEABF_4$/EiPS at high voltage and different temperatures from 20 to 80 °C. The results show that 0.5 M $TEABF_4$/EiPS electrolyte featured high electrochemical and thermal stability, allowing EDLCs to operate at high voltages from 3.0 V to 3.4 V at 60 °C and 80 °C. At 20 °C, 90% and 74% of the initial capacitance of EDLCs with $TEABF_4$/EiPS were retained after 500 h of floating at 3.4 V and 3.6 V, respectively. This superior stability is one of the highest reports of laboratory-scale $TEABF_4$-based EDLCs and is much higher than AN-based $TEABF_4$ electrolyte. In addition, the devices retained 68% of their original capacitance after floating at 3.4 V at 60 °C for 500 h, while devices using $TEABF_4$/electrolytes were unstable under these conditions. Based on a postmortem GC–MS analysis of the $TEABF_4$/EiPS electrolyte, no soluble decomposition products were found from the solvent, and the post-mortem

X-ray photoelectron spectra (XPS) analysis of the electrodes revealed the accumulation of non-soluble decomposition compounds on the electrode surface at high temperatures. The electrochemical reactions on the electrode surface were confirmed, including cation degradation via Hofmann elimination, the fluorination of the carbon surface, the in situ formation of HF, and the decomposition of EiPS. Based on the characterization results, the high electrochemical stability was attributed to the deposition of EiPS decomposition products on the electrode surface, which might act as a passivation layer to inhibit further degradation (Figure 5).

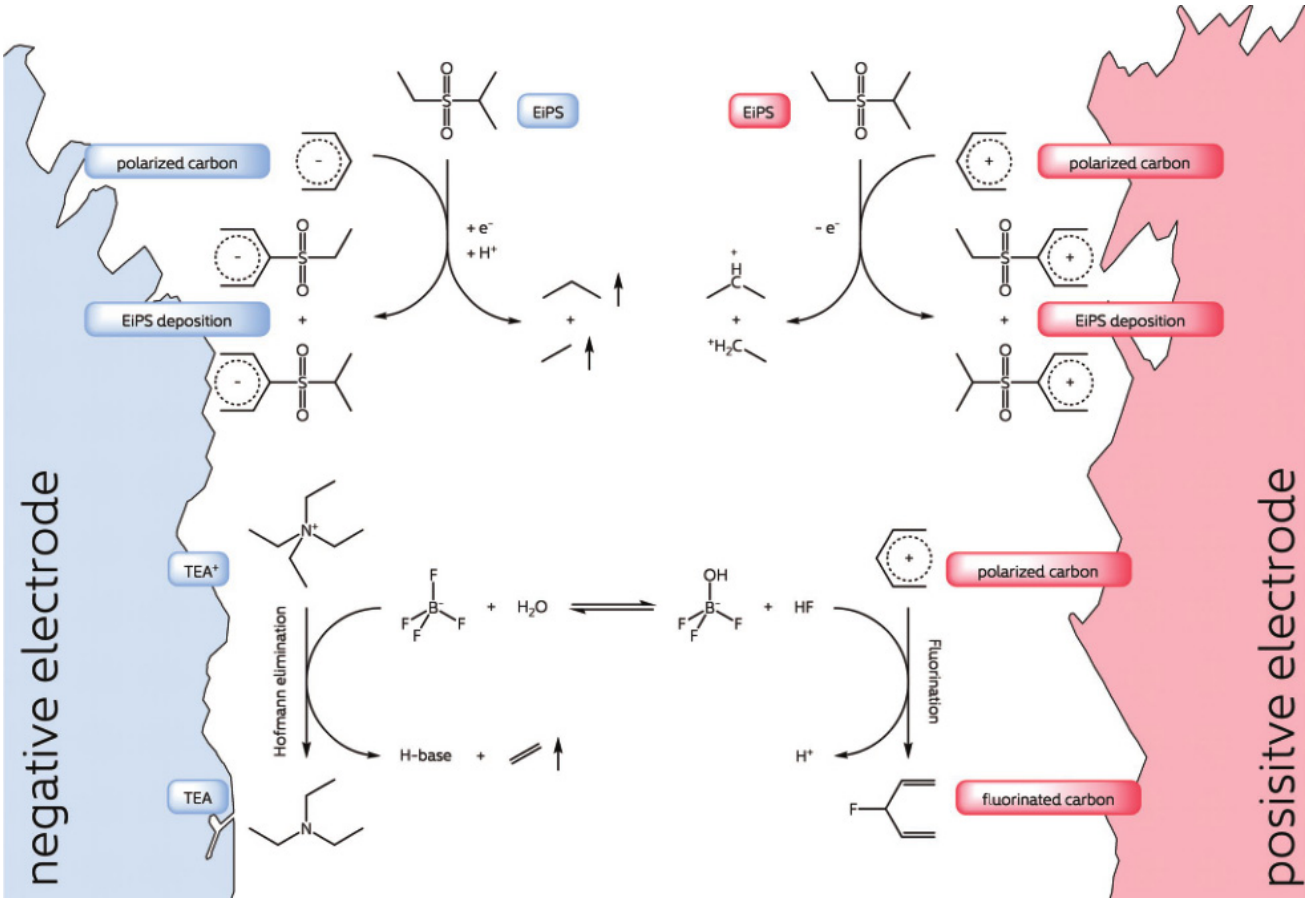

Figure 5. Proposed aging processes occurred on the interphase between $TEABF_4$/EiPS electrolyte and activated carbon electrodes at elevated temperatures [83].

Butylene carbonate (BC) is similar to PC in reduction stability and has higher oxidative stability than PC. Therefore, BC has higher electrochemical stability than PC and is a potential high-voltage alternative solvent of PC. BC has some isomers, including BC, 2,3–BC, and 1,2–BC. The boiling point of 2,3–butylene carbonate (BC) [84] is higher (243 °C) than that of PC. A spiro-(1,10)-bipyrrolidinium tetrafluoroborate ($SBPBF_4$)/2,3–BC electrolyte showed a voltage window of 3.5 V, far exceeding the PC-based electrolyte (2.7 V). The interface stability at high voltage was explained by the fact that the 4th and 5th positions provided a high-level protection from the external environment. This protective effect made these sites less vulnerable to attack by compounds that decompose the electrolyte (such as H_2O). Furthermore, 1,2–Butylene carbonate, as the isomer of 2,3–BC, also worked as alternative for PC [85]. The use of 1.5 M $Pyr_{14}BF_4$/1,2–BC allowed EDLCs to operate at 3.15 V, and the capacitance retention reached 90% after 500 h of floating.

Propionitrile (PN) has a higher boiling point (97 °C) and a lower melting point (−93 °C) than AN [86]. Nguyen et al. [87] reported the utilization of 1.0 M $SBPBF_4$/PN and N, N-dimethyl pyrrolidinium tetrafluoroborate ($DMPBF_4$)/PN as EDLC electrolytes and com-

pared their performances with 1.0 M $DMPBF_4$/AN and $SBPBF_4$/AN electrolyte. The PN-based electrolytes exhibited high electrochemical stability, low viscosity, good ionic conductivity, and excellent anodic potential limit. The symmetrically stable electrochemical windows of alternative electrolytes helped to protect these electrolytes from decomposition when charged to high oxidation potentials. Consequently, EDLCs using 1.0 M $DMPBF_4$/PN and $SBPBF_4$/PN electrolytes were cycled over 10,000 times at 3.5 V and 1000 h at 3.3 V. The $DMPBF_4$/PN electrolyte enabled EDLCs to achieve the highest power density (22.9 kW kg^{-1}) and energy density (49.3 Wh kg^{-1}). Otherwise, adiponitrile (ADN) also worked as an alternative solvent of AN due to its high boiling point (295 °C) and high flashpoint (163 °C). The voltage of EDLCs using 1.75 M $Pyr_{14}BF_4$/ADN electrolyte [88] ranged from 3.2 V to 3.7 V, and the capacitance retention of devices reached 81% at 3.7 V after 100,000 cycles (at 5 A g^{-1}). The operating voltage of EDLCs reached 3.4 V when galvanostatic charge-discharge processes were performed at room temperature as well as 60 °C, while that of EDLCs reached 3.0 V in the float tests. The temperature-programmed desorption and nitrogen adsorption analysis of the aged electrodes proved that the primary factor contributing to the degradation of EDLC performance was the formation of surface functional groups, which led to the gradual blockage of pores. Nevertheless, electrolytes using these nitrile solvents exhibit elevated viscosity and reduced conductivity compared to AN, thus constraining the power performance of the EDLCs.

It is noted that the use of some new solvents with high electrochemical stability indeed improves the voltage window of the IL–solvent electrolytes. However, due to their high viscosity and low ionic conductivity, this is usually accompanied by a reduction in power output.

3.3. Adding Co-Solvents to AN or PC for High Voltage

Co-solvents are often employed to adjust macroscopic properties of electrolyte components, including viscosity, dielectric constant, and melting point [89]. Electrolytes with multi-solvent systems demonstrate broad tolerances owing to the co-solvent's relatively lower viscosity and higher dielectric constant [90]. AN works as the widely used solvent for EDLC electrolyte, as the co-solvent can improve the electrochemical stability of AN-based electrolyte. As mentioned earlier, EDLCs utilizing $TEABF_4$–EiPS electrolyte achieved an operating voltage window of 3.4 V [83]. Balducci et al. [53] used AN and EiPS as mixed solvents to prepare 1.0 M $TEMABF_4$/EiPS/AN electrolyte. It was found that the operating voltage of the electrolytes using EiPS and AN (75:25 and 50:50) as co-solvent was 3.0 V, and the electrolyte system with EiPS/AN (75:25) showed excellent cycle and floating stability. In fact, EDLCs using the electrolyte with a 75:25 ratio exhibited only a 3% loss of initial capacitance after a 500 h cycles test at 3.0 V. Lang et al. [91] found that incorporating methyl acetate (MA) into $EMImBF_4$/AN can improve the performance of EDLCs at low temperature. The optimal pairing of an APDC electrode with the $EMImBF_4$/AN/MA electrolyte allowed the EDLCs to operate normally at –50 °C and exhibited an operating voltage of 3.5 V, a maximum power density of 26 kW kg^{-1}, a maximum energy density of 80 Wh kg^{-1}, and a long cycle lifespan of 10,000 cycles. Subsequent studies found that adding a fluorinated ether, 1,1,2,2–tetrafluoroethyl–2,2,3,3–tetrafluoropropyl ether (TTE), into $TEABF_4$/AN electrolyte could improve the stability of the electrolyte. As a result, a high working voltage of 3.6 V was assembled, which was much higher than the typical working voltage of 2.7 V for AN-based electrolytes without TTE [92]. In addition, the leakage current of $TEABF_4$–TTE/AN was smaller than that of electrolyte without TTE at the same charging voltage, and no decomposition of electrolyte was observed at 3.6 V. When charged to 3.6 V, the open-circuit voltage of ELDC with $TEABF_4$–TTE/AN decayed by 2.03 V after 24 h, which was lower than that of the EDLC without TTE (2.60 V). A mechanistic analysis indicated that cell self-discharge with the TTE additive was slowed down, which could be attributed to the inhibition of the faradaic reaction process caused by electrolyte decomposition.

As a common solvent for EDLCs with organic electrolyte, PC has higher electrochemical stability and better safety than AN, but its electrical conductivity is lower than AN. Thus, the electrochemical stability and conductivity of IL/PC-based electrolytes also need to be improved by adding other solvents. A common linear ether, 1,2–dimethoxyethane (DME), which has favorable chemical/electrochemical stability and quite low viscosity, has also been as a co-solvent for PC to enhance the transport behavior of ions. The EDLCs assembled with $EMImBF_4$–PC–DME (PC: DME = 1:1) electrolyte [93] had a voltage of 3.0 V and the property of fast charge-discharge. Ethylene carbonate (EC) has lower viscosity and a higher dielectric constant than PC. Dimethyl carbonate (DMC) has a linear structure, and its viscosity and melting point are significantly lower than those of ethylene carbonate (EC). For instance, the dielectric constants of propylene carbonate (PC), DMC, and EC are 65, 3.1, and 90 V/m, respectively, while their viscosities are 2.5, 0.6, and 1.9 mPa s, respectively. Therefore, the adding of DMC or EC into PC-based electrolyte is beneficial to the preparation of advanced electrolytes with high electrical conductivity and low viscosity [94]. The electrolytes containing $SBPBF_4$ with a solvent mixture of PC/DMC/EC (1:1:1 in volume) and PC/DMC (1:1 in volume) were studied for EDLCs [95]. The PC/DMC system exhibited the lowest viscosity (3.14 mPa s), while the PC/DMC/EC system showed the highest conductivity (18.08 mS cm^{-1}). Additionally, $SBPBF_4$ using a solvent mixture of the PC/DMC/EC system exhibited a stable voltage of 3.2 V and superior rate performance. In addition, the monofluorination of carbonates can increase relative permittivity and kinematic and dynamic viscosity. The dynamic viscosity of fluoroethylene carbonate (FEC) at 40 °C (4.1 mPa s) is higher than that of PC at 25 °C (2.53 mPa), and the relative dielectric constant of FEC at 40 °C (78.4) is higher than that of PC at 25 °C (64.92). Jänes et al. [96] introduced FEC as the co-solvent to construct FEC/PC solvent mixtures in various volume ratios. The EDLCs assembled with 1M $(C_2H_5)_3CH_3NBF_4$/FEC:PC (1:19) (5 vol.% FEC) and microporous TiC–CDC electrodes reached a voltage of 3.0 V. Therefore, the co-solvent in the above IL–PC system could reduce the viscosity or freezing point of electrolyte and slightly increase the voltage window.

From the above examples, it can be seen that co-solvents are mainly eaters, and there are few types of co-solvents reported at present. The co-solvent can slightly enhance the voltage window of the IL–AN (PC) electrolyte, and the main promotion effect is the improvement of other electrochemical properties, such as the increase in conductivity to improve the rate performance or low–temperature performance, which also are the important factors of EDLCs.

3.4. The Use of Solute Salt Additives for High Voltage

The ions of the solute salt play a direct role in forming the electric double layer, so the selection of solute salts is crucial for developing advanced EDLCs [97,98]. Encouragingly, it is of practical significance to study the IL–solvent electrolyte additives that can improve the operating voltage for improving energy density. F-containing compounds can form an effective passivation layer on the electrode surface, thereby minimizing the decomposition of solvent or AN polymerization. Back in 2005, Ishikawa et al. [99] reported that the cathodic stability of $EMImBF_4$ could be expanded by adding $LiBF_4$. Compared with $EMImBF_4$ and $TEMABF_4$/PC, $EMImBF_4$+$LiBF_4$/PC had a higher electrochemical stability window. They later confirmed that the enhancement of cathodic stability in the $LiBF_4$/$EMImBF_4$ system was associated with an "inhibiting effect" caused by the presence of Li^+ ions, rather than the "coating effect" from the formation of SEI [100]. The protective impact of Li^+ ions helped in curbing the side reactions on the AC electrode. Li et al. [101] used $LiFP_6$ as an additive to prepare the $EMImBF_4$/$LiPF_6$/PC/DMC electrolyte, which had a low viscosity of 2.89 mPa s, a high ionic conductivity of 20.72 mS cm^{-1}, and high electrochemical stability. The inhibiting effect brought by Li^+ effectively hindered the reduction of cations in IL. The advanced 3V-class EDLCs were successfully constructed using this electrolyte, and their comprehensive performance was obviously better than that of EDLCs using pure $EMImBF_4$ or $EMImBF_4$/solvent, with a capacitance retention of 95.8% after 20,000 cycles

at 3.0 V. The improvement of the overall performance was primarily attributed to the improved ion transport capacity, the balance charge storage of the electrodes, and the passivation of the electrode surface, which were caused by the combined action of Li salt and carbonate solvent.

Krause et al. [102] reported fluorinated additives such as ethyl(2,2,2–trifluoroethyl) carbonate (ETFEC), (2,2,2–trifluorothyl) methyl carbonate (TFEMC), lithium difluoro(oxalate) borate (LiDFOB), bis(2,2,2–trifluorothyl) carbonate (bTFEC), and tris(2,2,2–trifluoroethul) phophite (TTFEPi) for the $SBPBF_4$/AN system. The results demonstrate that LiDFOB and ETFEC could improve the stability at high voltage (>2.7 V). In particular, when 2 wt% LiDFOB additive was added to $SBPBF_4$/AN, the resulting EDLC cells revealed good capacitance retention and reduced internal resistance in the voltage ranges of 3.5 to 4.0 V (Figure 6). In addition, EDLCs using TTFEPi showed lower self-discharge performance. The electrochemical decomposition degree of the internal components of the cell was reflected by the steady-state current value. The cell with TTFEPi additive showed the lowest current value in the test, indicating that TTFEPi might reduce aluminum corrosion at high voltage to improve the coulombic efficiency.

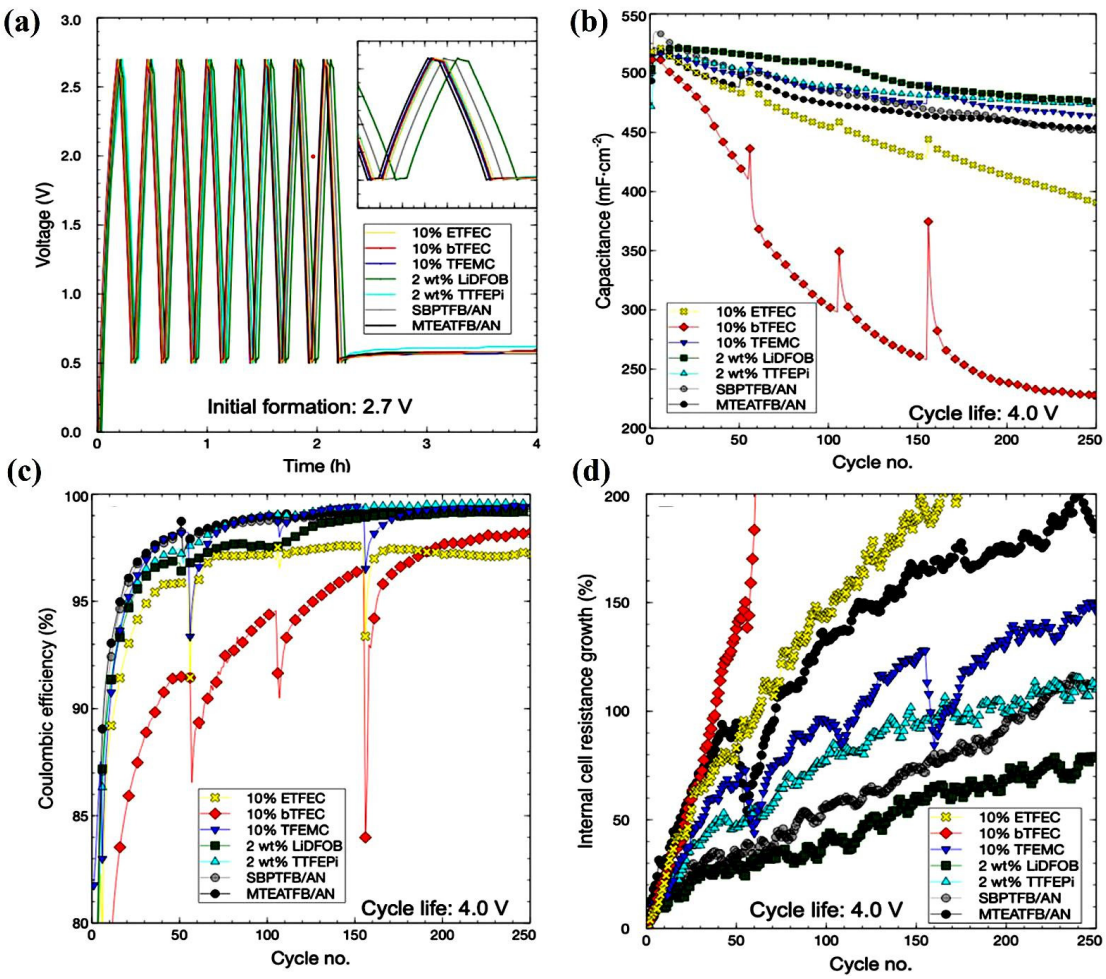

Figure 6. (**a**) Eight constant current charge/discharge cycles at a current of 5 mA across a voltage range of 0.5 to 2.7 V. (**b**) Capacitance of EDLCs during cycle life testing across a range of 0.5 to 4.0 V. (**c**) Coulombic efficiency of EDLCs under a voltage range of 0.5 to 4.0 V cycle life. (**d**) Increase in internal resistance as determined by current interrupting a voltage range of 0.5 to 4.0 V in cycle life test [102].

Besides the F-containing compounds, different kinds of ILs can also be used as the additives for IL-based electrolytes. In addition to the organic solvent with high dielectric constant and minimal viscosity, incorporating ILs with other cations can also improve the electric conductivity and reduce the viscosity of IL-based electrolytes. Adding different contents of $EMImBF_4$ to 0.2 M $SBPBF_4$/PC/DME [103] electrolyte reduced the interfacial resistance and bulk resistance, thereby increasing the ionic conductivity. In particular, the electrolyte with 15 vol% $EMImBF_4$ showed superior capacitance, electrochemical stability, ionic conductivity, and low interfacial resistance. Moreover, when 15 vol% $EMImBF_4$ was added, the XPS spectra confirmed the thinnest SEI film. Otherwise, adding $EMImBF_4$ or EMImTFSI as additive into $TEABF_4$/PC [104] also improved the ionic conductivity and stability by inhibiting electrolyte decomposition. The ESWs of the electrolytes with IL additive were wider than that of the conventional electrolyte, which enabled EDLCs to operate stably at 3.7 V. When the amounts of $EMImBF_4$ and EMImTFSI were 7 wt.%, the specific capacitances of the initial value of EDLC after 10,000 cycles were 97.5% and 91.3%, respectively. By mixing N–butyl–N–methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr_{14}TFSI) and trimethyl propylammonium bis(trifluoromethanesulfonyl)imide (TMPATFSI) with an equivalent mole ratio into AN at 1.0 M concentration [105], the binary IL electrolyte exhibited a low viscosity of 0.692 mPa s^{-1}, an exceptional electric conductivity of 44.3 mS cm^{-1}, and a wide electrochemical stability window of 4.82 V. EDLCs constructed with AC electrodes and this binary ILs electrolyte achieved an elevated operating voltage of 3.1 V, a maximum power density of 32.16 kW kg^{-1}, and a maximum energy density of 28.30 Wh kg^{-1}. These metrics were notably superior compared to those of commercially available EDLCs using organic electrolytes.

Unlike the common ILs, which can improve the conductivity and reduce the viscosity of the electrolyte by cationic regulation, functional ILs with large-sized groups can enlarge the operating voltage window by adjusting the polarization limit of the electrode. The operating voltage of EDLCs is determined by the upper limit potential (P_U) and lower limit potential (P_L), which correspond to the potential of oxidation and reduction of electrolyte, respectively. By adding a silica-grafted ILs additive into the EMImTFSI/PC electrolyte, Yan et al. [106] developed an effective strategy to adjust the polarization potential of electrodes and improved the potential limits of the positive and negative electrodes of EDLCs (Figure 7a). Compared with the electrolyte without additives, the electrolyte with 10% SiO_2–IL–TFSI exhibited a more symmetric potential range for two electrodes, and the P_{0V} was adjusted to ~0 V vs. Ag. In this case, P_U and P_L were expanded to 1.6 and −1.6 V vs. Ag in a three-electrode system, and the voltage of the AC-based EDLCs increased from 2.8 to 3.2 V. The energy density was increased by 39% with the improvement in cycle stability. Subsequently, a polymeric imidazole IL with ether branch (PVEImTFSI) was synthesized and worked as an additive to EMImTFSI/PC. It was found that PVEImTFSI could also enlarge the limit potential ranges of carbon-based EDLC [107]. The addition of PVEImTFSI improved the electrochemical stability and effectively adjusted the upper limit potential (P_U) and lower limit potential (P_L) of the electrolytes. The P_U and P_L of electrolytes with 10% PVEImTFSI reached 1.7 and −1.5 V vs. Ag. The working voltage of EDLCs with 10% PVEImTFSI was increased to 3.2 V compared with EDLCs at 2.8 V without additives. As a result, the energy density was increased by approximately 41.5%. The cycling stability of EDLCs with electrolyte containing 10% PVEImTFSI at 3.0 V and 3.2 V was also significantly enhanced. In addition, the equivalent circuit model was simulated and the Bode plots were proposed according to the results of electrochemical impedance spectroscopy (EIS). Both simulated and measured date show that the resistance of each element was reduced by adding PVEImTFSI, which improved the ion dynamic and reduced the energy barrier of the ion diffusion, thereby improving the electrochemical performance of EDLCs (Figure 7b).

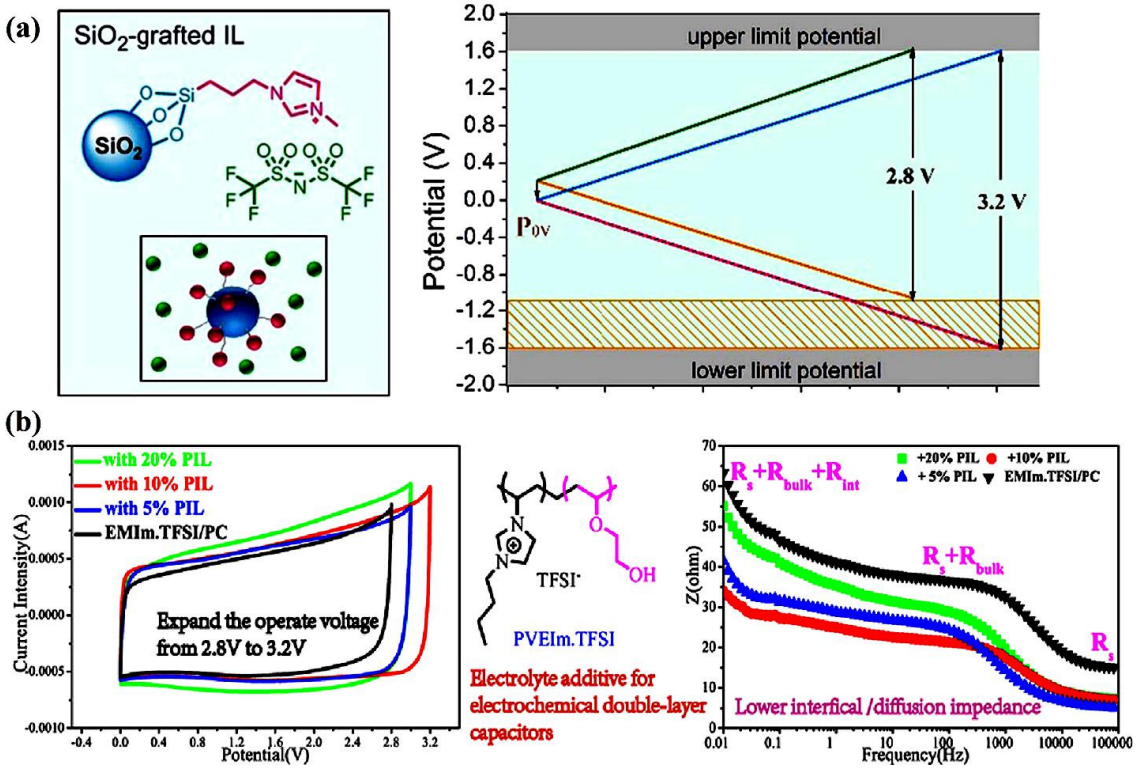

Figure 7. (**a**) The structure of SiO_2–IL–TFSI and the schematic of increasing the operational potential [106]; (**b**) chemical structure of PVEImTFSI and its positive effects on voltage and impedance [107].

Moreover, novel electrolytes for EDLCs were prepared by adding cetyltrimethylammonium-bromide-grafted Ti_3C_2 MXene (Ti_3C_2–CTAB) into $EMImBF_4$/PC and Et_4NBF_4/-PC [108]. Remarkably, the ionic conductivity of electrolyte with the Ti_3C_2–CTAB additive increased by 38%, and the solid–liquid surface energy decreased from 18.03 mN m^{-1} to 12.37 mN m^{-1}. The hydrogen bonds and electrostatic force generated between Ti_3C_2-CTAB and $EMImBF_4$ promoted the dissociation and ion transfer of electrolyte ion pairs. Comparing with free-additive electrolyte, the EDLCs assembled with 0.5% additive showed higher rate capability (76.4% vs. 45.8%), higher specific capacitance (29.6 F g^{-1} vs. 21.6 F g^{-1}), and longer cycling life after 9000 cycles at 3.0 V (83.6% vs. 59.8%). The addition of Ti_3C_2–CTAB reduced the interfacial resistance of electrolyte/electrode, which improved the electrochemical performance. Consequently, EDLCs based on Ti_3C_2–CTAB/$EMImBF_4$/PC obtained a high energy density of 28.3 Wh kg^{-1} and a power density of 18.3 kW kg^{-1}.

It can be seen from the results reported above that there are many kinds of solute additives, including F-containing compounds, ILs, and ionic compounds with large-sized groups. The effect of adding these additives is immediate, so the addition of solute additives is a very effective and relatively simple way to achieve high voltage. However, designing or selecting suitable additives is still a challenge.

4. Conclusions and Future Perspectives

EDLCs have become important energy storage devices to improve the power quality of renewable energy because of their fast energy storage and high power output. As mentioned above, the electrochemical stability window is an important factor restricting the energy density of EDLCs. The development of electrolytes with wider electrochemical windows is an important direction for constructing high-energy-density EDLCs. IL–solvent electrolytes are the most commercially promising for EDLCs due to their moderate conductivity and electrochemical window. In the past few years, many efforts have been dedicated to the study of new solvents and electrolyte salts to achieve high-voltage EDLCs.

This review provides insights to expand the working window from the IL–solvent component level. In summary, tuning the components of the IL–solvent electrolyte is an effective method to broaden the voltage window of EDLCs with IL–solvent electrolytes. Various excellent organic IL electrolytes have been developed, including those that have increased IL concentration, those that have novel organic solvents with high electrochemical stability, and those that have co-solvents and solute salt additives in their electrolytes. The as–discussed high-voltage IL–solvent electrolyte components and their electrochemical performances are summarized in Table 2. Studies show that the voltage of EDLCs with the use of these electrolytes increased compared to that of the initial. The results indicate that the electrolyte salts, solvents, and additives have strong effects on the electrochemical voltage window and the properties of the interface. Despite the fact that some progress has been made in the research of IL–solvent electrolytes, there are still some works to be carried out in order to meet their practical applications. The future research of IL–solvent electrolytes will involve the following considerations:

Table 2. The methods to achieve high voltage of EDLCs with IL–solvent electrolytes.

Tuning Methods	Electrolytes	Voltage (V)	Ref.	Challenges
High salt concentration	2M $Pyr_{11}BF_4$/AN	3.4	[75]	High viscosity and high cost limit the commercial application
	2.3M Pyr_{14}TFSI/PC	3.5	[51]	
	$EMIMBF_4$/AN or PC or γ-butyrolactone (0.005–1.0 M solvent)	3.2	[77]	
High stable solvent	$TEABF_4$/EiPS	3.4	[83]	Accompanied by a reduction in power output
	$SBPBF_4$/2,3-BC	3.5	[84]	
	$Pyr_{14}BF_4$/1,2-BC	3.15	[85]	
	$SBPBF_4$/PN	3.5	[87]	
	$DMPBF_4$/PN	3.3	[87]	
	$Pyr_{14}BF_4$/ADN	3.4	[88]	
Co-solvent	$TEMABF_4$/EiPS/AN	3.0	[53]	The increase of voltage window is limited
	$EMImBF_4$/MA/AN	3.5	[91]	
	$TEABF_4$/TTE/AN	3.6	[92]	
	$SBPBF_4$/DME/PC	3.2	[95]	
	$(C_2H_5)_3CH_3NBF_4$/FEC/PC	3.0	[96]	
Solute salt additive	$EMImBF_4$/$LiPF_6$/PC/DMC	3.0	[101]	The designing and selecting suitable additives lack systematic guidance
	$SBPBF_4$/LiDFOB/AN	4.0	[102]	
	$TEABF_4$/$EMImBF_4$/PC	3.7	[104]	
	Pyr_{14}TFSI/TMPATFSI/AN	3.1	[105]	
	EMImTFSI/SiO_2-IL/PC	3.2	[106]	
	EMImTFSI/PVEImTFSI/PC	3.2	[107]	
	$EMImBF_4$/Ti_3C_2CTAB/PC	3.0	[108]	

(1) It is necessary to develop high-purity, newly low-cost IL salts with high electrochemical stability windows. Firstly, the structure innovations of IL electrolyte salts with high surface ion density are carried out by the cation structure regulation strategy. Secondly, the purity of IL should be taken into account. It is well known that a small number of halides or water may influence the physicochemical properties of electrolytes and the behavior of EDLCs significantly. Thirdly, the cost is the major consideration while using IL in commercial applications. It is necessary to explore the development of simple and atom-economic synthesis methods with low-cost raw materials and post-treatment purification steps, which make the IL a cheap solute. Finally, the strong effect of innovation on IL–solvent electrolytes on the structure and the formation of the double layer is necessary to study. Among the several aspects, the influences of the solvation process and ion mobility need to be analyzed, which will indicate the advantages and limitations of innovative electrolyte components.

(2) We must continue to screen novel organic co-solvents with high dielectric constants, wide temperature ranges, low costs, and low toxicities to improve the electrochemical stability of EDLCs. Nevertheless, in some AN systems, the increase in voltage is obtained at the expense of power reduction. Therefore, it is necessary to carry out research on the tuning technology of multi-solvent components and explore the synergistic mechanism between the components. Considering that the high electrolyte concentration and highly stable alternative solvents in the above strategies can increase the voltage window and that additives and co-solvents can also increase the conductivity, the combination of these strategies can develop a high-concentration ionic liquid–mixed solution electrolyte to achieve a synergistic effect in high-performance EDLCs.

(3) The selection and design of solute additives still remain a major challenge. Large-cation ILs are the main research content of large-size salts as IL additives, and the rarely involved anions may be a future direction. Meanwhile, it is necessary to analyze the influence of solute additives to the functional groups on the electrode surface, which will allow us to deeply understand the advantages of electrolyte components and the enhanced mechanisms.

(4) As the microscopic reaction of the electrode–electrolyte interface occurs in the Stern layer of the electric double layer, which is determined by the ion dynamics and physicochemical interactions, theoretical study of the formation, thickness, and composition of the Stern layer will be the focus of research in the field of high voltage. The ionic interaction and kinetics of the IL–solvent system at the electrolyte/electrode interface should be systematically studied using molecular dynamics simulations. The influence mechanisms of ion size and solvation on the formation and thickness of the Stern layer in the electric double layer also need to be systematically studied via simulation. In addition, it is necessary to introduce an effective computational screening method to identify ILs, solvents, and additives suitable for EDLCs.

(5) A clear understanding of the electrochemical degradation mechanism of the IL–solvent electrolyte of EDLCs at high voltage is still lacking at present, which gives important guidance for the design of IL–solvent components with a wide operating window. The inhibition of electrochemical reactions on the electrode surface caused by the electrolyte components requires a deep understanding so that a highly electrochemical stable electrolyte and an electrode material with a stable surface can be designed.

Author Contributions: Y.W.: investigation, writing—original draft, methodology, funding acquisition; K.X.: investigation, formal analysis; X.Z.: investigation, formal analysis; C.Y.: funding acquisition, formal analysis; Y.L.: funding acquisition; K.S.: review—editing; P.M.: supervision—review, funding; S.W.: supervision—review; J.L.: supervision, funding acquisition, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Taishan Scholars Program, No. tsqnz20230629; the Western Young Scholars Foundations of Chinese Academy of Sciences; the Science Fund of Shandong Laboratory of Yantai Advanced Materials and Green Manufacturing, No. AMGM2022A02, AMGM2023A04; the Collaborative Innovation Alliance Fund for Young Science and Technology Worker, No. HZJJ23-5; and the FAW Volkswagen China Environmental Protection Foundation Automotive Environmental Protection Innovation Leadership Program.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

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