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Recent Progress of the Application of Electropolymerization in Batteries and Supercapacitors: Specific Design of Functions in Electrodes

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Electrochemical energy storage devices play a vital role in human life, and the requirements for their sustainability and environmental friendliness have been increasing in recent years. Electropolymerization, as a convenient method for polymer synthesis, has attracted increasing attentions in applications in the field of energy storage and conversion. It is not only commonly employed for the fabrication of various self-supporting electrodes, but also is one of the most promising preparation strategies for organic electrode materials, internal interlayers within electrodes, functional protective layers, and current collector surface modifications. Previously published works have confirmed that the introduction of electropolymerization can effectively improve the electrochemical performance of various energy storage devices. However, there are still challenges in the universality of the synthesis route, in-depth understanding of interface chemical behavior, and scaled-up production. This mini review summarizes the main components in electropolymerization, material synthesis mechanisms, and their application principles in batteries and supercapacitors. Additionally, the current challenges and future development directions of electropolymerization have been discussed, offering some perspectives for further exploration.

1. Introduction

Energy storage devices represented by batteries and supercapacitors are becoming increasingly important for the development of human society. On one hand, the application of energy storage devices greatly enhances the efficiency of harnessing unpredictable renewable energy sources from nature, such as solar energy, wind energy, tidal energy, etc., reducing the impact of natural environmental factors on human life.[1] On the other hand, the stability and reversibility of energy storage devices have propelled the rapid advancement of cutting-edge electronic devices like smartphones, drones, electric vehicles, etc., bringing convenience and enriching daily life.[2]

Higher energy density and longer lifespan have always been the relentless goals in the pursuit of energy storage devices. The electrode is the most crucial component in energy storage devices. The electrode materials, their structure, and preparation methods all have an impact on the performance of energy storage devices. In order to eliminate the use of non-active materials (e.g. binders and conductive additives), reduce electrode mass, and enhance electrode energy density, self-supporting electrodes have gained widespread attention in research and development.[3]

Self-supporting electrodes do not require additional support materials or carriers, reducing electrode complexity and preparation costs. Self-supporting electrodes typically exhibit good electrical conductivity, enabling efficient electron transfer, thereby improving the efficiency of electrochemical reactions. In addition, a self-supporting electrode is advantageous for in situ/operando analysis, allowing for a more intuitive and accurate understanding of the electrode's phase, morphology, and structural changes during charge and discharge processes without altering the electrode state or causing damage.[4,5] Methods for preparing self-supporting electrodes include hard templating,[6–8] electrospinning,[9,10] electropolymerization,[11] physical vapor deposition,[12] chemical vapor deposition,[13,14] and atomic layer deposition,[15] etc.

Among these methods, electropolymerization is a process that uses electrochemical techniques to form continuous polymer films or structures from dispersed monomers or polymers. The electropolymerization process can be precisely controlled, including parameters such as reaction time, poten-

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tial, or current density, to adjust the properties and structure of the resulting polymer. This means that the polymer thickness, porosity, pore size, morphology, and chemical properties can be optimized as needed. Electropolymerization typically yields uniform polymer films or structures which helps to ensure consistent performance throughout the entire surface or structure of the prepared material. Compared to the other preparation methods, electropolymerization is a straightforward process that does not require expensive equipment or complex procedures, resulting in relatively low preparation costs.

In addition to facilitating the preparation of self-supporting electrodes, electropolymerization can be employed to design and create protective layers on the external electrode surface,[16] develop intermediary layers between electrodes and separators,[17,18] or craft modifying layers for current collectors.[19] All these approaches are conducted externally to the electrode. Due to the inherent electric fields present during the operation of electrochemical devices, electropolymerization can also be carried out in situ within the electrode. This enables the design of various protective layers for electrode materials,[20,21] thereby enhancing the stability of the electrode materials.[22,23] Moreover, instead of electropolymerization of individual organic monomer, researchers have developed electropolymerization with double organic monomers to prepare a kind of hydrogel materials with large specific surface area and well-designed electron transfer route as well as ion transfer route.[24] Furthermore, inorganic electrodeposition can be integrated withorganic electropolymerization, enabling both processes to occur simultaneously, to fabricate hybrid inorganic-organic metal protective layers.[25] Expanding this strategy to the realm of energy storage devices, protective layers for battery electrodes have been developed.[18] Apart from organic monomers, electropolymerization of coordination polymers[26] and conductive fullerene polymers[27] has also been explored. The development of these novel strategies significantly broadens the application scope of electropolymerization.

The discovery of conducting polymers is of great historical significance to electropolymerization. Since A. J. Heeger, A. G. MacDiarmid and H. Shirakawa discovered in the 1970s that polyacetylene doped with bromine has a conductivity of a million times higher than that of pristine polyacetylene, a huge breakthrough was made in the development of conducting polymers. Subsequently, conducting polymers attaining great practical application potential have attracted plenty of attention.[28] Various conducting polymers including poly (thiophene), polyaniline, polypyrrole, poly (3,4-ethylenedioxythiophene) and so on have been synthesized and investigated. The 1980s witnessed further advancements in the synthesis and understanding of conducting polymers. Techniques for processing and doping were refined, leading to improvements in electrical conductivity and stability. The properties of conducting polymers (e.g. conductivity, thickness and morphology) dependent on the factors such as solvent, supporting electrolyte, voltage and temperature have been widely investigated and concluded by several classical handbooks and encyclopedia, for instance Handbook of Conducting Polymers by T. A. Skoteheim (1986) and Handbook of Organic Conductive Molecules and Polymers by N. Singh Nalwa (1997).[29,30] The 1990s saw a surge in research on conducting polymers for practical applications. Due to the possession of various proper-

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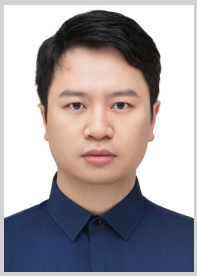

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ties such as high electrical conductivity, good magnetic property, high optical property, light weight and so on, efforts were made to develop conducting polymer-based devices including light emitting diodes, solar cells, sensors, microelectronics and so on.[31] Research in the 2000s focused on enhancing the performance and stability of conducting polymers, especially for applications in flexible electronics and bioelectronics. New approaches, including the development of composite materials and novel polymer structures, were explored to address challenges such as low processability and environmental instability. Nowadays, with the fast development of energy storage devices including batteries and supercapacitors, conducting polymers have also gradually found their specific application in them. As one of the most universal methods for synthesizing conducting polymers in recent decades, electropolymerization has greatly promoted the widespread use of conducting polymers.

Though there are some review and perspective articles on electropolymerization available, the vast majority of them are devoted to the research progress of electropolymerization in applications such as corrosion protection for metals,[32,33] high-resolution OLEDs,[34] electrochemical sensors,[35] and biosensors.[36] With the flourishing development of batteries and supercapacitors, and the widespread exploration of electropolymerization in electrochemical devices, there is a lack of review article introducing and discussing the relevant research progress in this context. Given the numerous advantages of electropolymerization in electrode preparation, it is essential to review its research progresses in batteries and supercapacitors. This not only helps identify current issues in electropolymerization but also provides further guidance for the development of new electrode materials and electrode systems for future application. In this mini review, we introduce the application of electropolymerization in batteries and supercapacitors through two main sections. The first section introduces the main components in electropolymerization process, including monomers in the application of batteries and supercapacitors, selection principal of substrates and solvents, the morphology-performance relationship of the electropolymerization created materials, and the specific characterization methods for electropolymerization. Their application in batteries (e.g., organic batteries, lithium-ion batteries (LIBs), lithium-sulfur batteries (LSBs), zinc-ion batteries (ZIBs)) and supercapacitor has been classified in the second section. It focuses on elucidating the application principles of electropolymerization, the polymerization mechanisms of materials, and their performance in each context. Finally, we also summarize with perspectives on the challenges and future research directions of electropolymerization in electrochemical devices.

2. Synthesis and Characterization in Electropolymerization

Electropolymerization is a process that utilizes electrochemical methods to synthesize polymeric compounds on the surface of conductive substrates, which is a mature technique for the preparation of polymers for decades. In the operational process, a potential is applied to the electrode, causing electrons and/or ions to flow through the electrolyte solution. At the electrode surface, monomer molecules are excited by the applied potential, undergoing oxidation-reduction reactions. In the oxidized state, monomer molecules form positive ions or excited states, which then react with other monomer molecules. The excited monomer molecules gradually polymerize on the electrode surface, forming polymer chains.[22,37] This polymerization usually occurs on the electrode surface that is infiltrated by the electrolyte solution, which in turn induces the attachment of polymer monomers and the gradual growth of polymer chains over time under a certain potential, eventually forming a continuous polymer film. During the synthesis process, the physical and chemical properties of the polymer can be controlled by adjusting finely parameters such as potential, current density, and solution composition. To provide a deeper understanding of the specific synthesis conditions for electropolymerization, the key aspects/components of electropolymerization (i.e., monomers, substrates, solvents, and voltage) have been described separately, as shown in Figure 1. The different morphologies induced by these key factors in electropolymerization synthesis have also been thoroughly evaluated and analyzed, as well as the electrochemical performance they endow energy storage devices with.

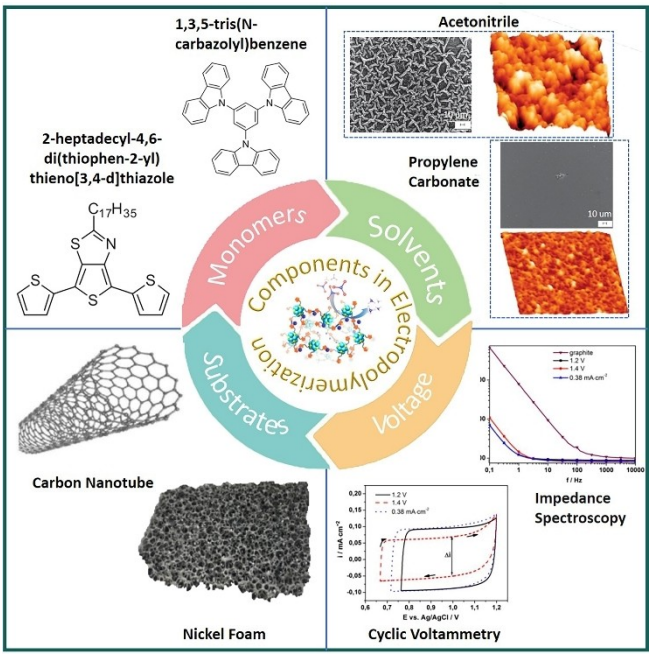

Figure 1. Main components (monomers, substrates, solvents, and voltage) in the process of electropolymerization. The morphology of poly(3,4-ethylenedioxythiophene) (PEDOT) prepared in acetonitrile and propylene carbonate, respectively (upper right corner). Reproduced with permission.[38] Copyright 2010, American Chemical Society. The cyclic voltammetry and impedance spectroscopy of the electropolymerization of PEDOT via different voltage and current conditions (lower right corner). Reproduced with permission.[39] Copyright 2015, Elsevier.

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2.1. Components

2.1.1. Monomers

Monomer is the most crucial factor, determining the success or failure of the polymerization process. According to the working principles of electropolymerization, monomer needs to possess certain conductivity. In addition, it should possess sufficient electrochemical stability to maintain stability in the electropolymerization reactions and to avoid side reactions, especially under high voltage or high current density conditions. The monomer should have good solubility to ensure complete dissolution in the electropolymerization solution and easy participation in the reaction. The reactivity of the monomer should be moderate, allowing it to undergo electropolymerization under the chosen conditions without overly vigorous reactions that could lead to side reactions or unstable products. Common organic monomers include thiophene,[20] pyrrole,[40–42] aniline,[19,43] and their derivatives.[4,23,44,45] In principle, the polymerization of the monomer should exhibit a certain level of controllability to regulate the molecular weight and distribution of the resulting polymer. Higher monomer concentrations generally lead to higher degrees of polymerization. Li et al. investigated the impact of monomer concentration on the electropolymerization of polypyrrole (PPy), revealing a proportional increase in electropolymerization current with the increase of monomer concentration. Product mass and time exhibited a linear correlation in different monomer concentration.[46] Due to the decrease in conductivity at the reaction interface with increasing electropolymerization time, the thickness of the product reaches a certain limit and no longer increases. Almog et al.[47] studied the relationship between film thickness and cycle number during the electropolymerization of polypyrrole (PPy) and found that after 30 cycles, the film thickness remained at 0.35 μm.

Recently, many new polymers such as conducting polymer hydrogel (CPH) and coordination polymers have been synthesized via electropolymerization. Conducting polymer hydrogels (CPH) is one of the derivatives of conducting polymers and is consisted with three-dimensional polymer network and large amounts of water medium. CPH has the both advantageous features of hydrogels and conductive polymers. In comparison with solid electrode materials created by the polymerization of traditional monomers, CPH can contact with the electrolyte solution closely at the molecular level due to the swelling behavior of polymer with water and ions. In this case the solid-state electronic transfer phase is completely surrounded by aqueous ionic transfer phase, ensuring a full utilization of active materials. CPH also consists of continuous interconnected electronic and ionic transfer routes. In combination with the flexibility, CPH has great potential in fabrication of flexible solid state energy devices such as supercapacitors.[24] Coordination polymers is made of metal ions and ligands. By selecting different metal ions and ligands, various coordination polymers could be fabricated easily. Compared with the polymers created by the polymerization of traditional monomers, the metal ions usually have catalytic activity, which accelerates the activation rate. In addition, there are large amounts of nanopores existing in coordination polymers, which significantly enhance the specific surface area of polymers.[26]

Electropolymerization is primarily used in batteries and supercapacitors to prepare organic electrode materials, as well as to construct protective layers or functional layers on electrodes. Additionally, researchers have employed electropolymerization to enhance the stability of organic electrode materials, prepare interlayers in batteries, and modify current collectors. The electropolymerization monomer applied in batteries and supercapacitors in recent years has been classified based on functional purposes and summarized in tabular form (Table 1, Table 2 and Table 3). Table 1 lists monomers of electropolymerization for preparing electrode materials in batteries and supercapacitors. Monomers used for preparing electrode materials typically possess a conjugated structure and a π-electron system, allowing them to accept or donate electrons, thereby undergoing redox reactions during electrochemical processes. For pure organic polymers as active materials of electrodes, the introduction of conductive fullerene can greatly improve the utilization efficiency of electrodes. In supercapacitors, the redox reactions of organic electrode materials contribute to a pseudocapacitance, enhancing the overall capacitance of the electrode. In organic lithium-sulfur batteries, the monomer often contains functional groups (e.g. thiol groups), which mitigate the formation of higher-order polysulfides and effectively address the shuttle effect at its source when reacting with metallic lithium.

Table 2 summarizes the reported monomers of electropolymerization for constructing electrode protective layers in batteries and supercapacitors. The common characteristic of these monomers is their ability to dissolve in the electrolyte of battery, enabling in situ polymerization within the electrode. The conjugated organic thin film formed after polymerization acts as a barrier, isolating the electrode material from direct contact with the electrolyte and enhancing the electrode stability. Meanwhile, the in situ formed film facilitates the charge transfer and conversion on the electrode, thereby improving the efficiency of electrochemical reactions.

Table 3 lists the monomers of electropolymerization for other functions in batteries and supercapacitors. In organic batteries, monomers can undergo in situ polymerization at lower voltages, achieving sufficient polymerization degrees through the initial few charge-discharge cycles. This significantly reduces the solubility of electrode materials in the electrolyte and enhances the stability of the electrode.

Table 4 lists the capacitive properties of some polymer materials formed via electropolymerization. In the construction of a composite electrode via electropolymerization, the capacitive properties of polymer products are important and necessary to be considered, especially for the design of supercapacitor electrodes, which directly affect the application potential. As shown in Table 4, the capacitance of polymers is related to multiple factors, such as monomer type, conductivity, dielectric constant, and electrode materials, etc. These factors interact with each other. Therefore, when designing and selecting conductive polymers for batteries or supercapacitors,

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Table 1. Monomers of electropolymerization for preparing organic electrode materials in batteries and supercapacitors.

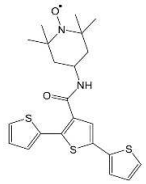
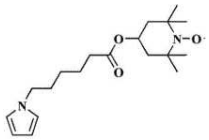
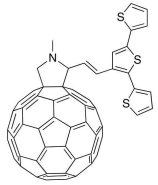
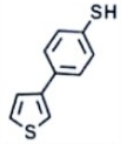
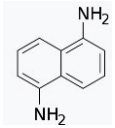
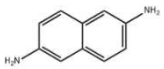
Monomer			Solvent	Substrate	Applications		Ref.
Monomer	Molecular formula	Molecular structure			Function	Device	
(2,2,6,6-tetramethylpiperidin-1-yl)oxyl	$C_{22}H_{25}S_3N_2O_2$		$CH_2Cl_2 + Bu_4NPF_6$	Carbon paper	Cathode materials	Organic batteries	[48]
Nitroxide free radical-contained pyrrole	$C_{19}H_{31}N_2O_3$		Acetonitrile	Conductive carbon fiber modified steel	Cathode materials	Organic batteries	[44]
N-methyl-2-(2-[2,20;50,200-terthiophen-30-yl]ethenyl)fullero [3,4]pyrrolidine	$C_{77}H_{15}S_3N$		Glassy carbon	Propylene carbonate	Cathode materials	Organic batteries	[27]
4-(thiophene-3-yl) benzenethiol	$C_{10}H_8S_2$		N_2-saturated acetonitrile	Ni foam	Cathode materials	LSBs	[4]
Pyrrole	C_4H_5N		Hydrochloric acid solution	Carbon nanotubes	Cathode materials	Aqueous Zinc-air batteries	[40]
1,5-naphthalenediamine	$C_{10}H_{10}N_2$		$ZnSO_4$ solution	Stainless mesh	Cathode materials	Aqueous ZIBs	[37]
2,6-naphthalenediamine	$C_{10}H_{10}N_2$		$ZnSO_4$ solution	Stainless mesh	Cathode materials	Aqueous ZIBs	[49]

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Table 1. continued

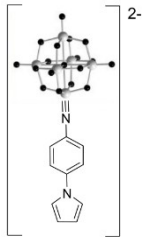
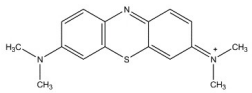
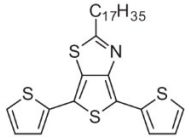
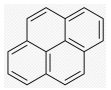
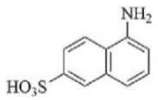
Monomer			Solvent	Substrate	Applications		Ref.
Monomer	Molecular formula	Molecular structure			Function	Device	
Oxometalates	$[NBu_4]_2$ $[Mo_6O_{18}NC_6H_4NC_4H_4]$		Acetonitrile	glassy carbon	Electrodes	Pseudocapacitors	[50]
Methylene blue	$C_{16}H_{18}ClN_3S$		Na_2SO_4 solution	Carbon fiber	Electrodes	Pseudocapacitors	[51]
2-heptadecyl-4,6-di(thiophen-2-yl) thieno[3,4-d]thiazole	$C_{34}H_{41}NS_4$		Dichloromethane	Glassy carbon	Electrodes	Pseudocapacitors	[45]
Pyrrole	C_4H_5N		Sulfuric acid solution	Cotton fabric	Electrodes	Pseudocapacitors	[41]
Pyrene	$C_{16}H_{10}$		Solvent-free	Activated carbon	Electrodes	Pseudocapacitors	[43]
Pyrrole	C_4H_5N		Urea + choline chloride	Graphite	Electrodes	Pseudocapacitors	[42]
Aniline	$C_6H_5NH_2$		Solvent-free	Activated carbon	Electrodes	Pseudocapacitors	[43]
5-amino-2-naphthalenesulfonic acid	$C_{10}H_6NSO_3$		$HClO_4$ solution	Carbon cloth	Electrodes	Pseudocapacitors	[52]
Aniline Phytic acid	$C_6H_5NH_2$ $C_6H_{18}O_{24}P_6$		H_2SO_4 solution	Gold coated polyethylene terephthalate (PET) film	Electrodes	Pseudocapacitors	[24]

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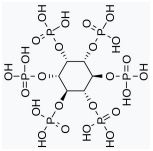
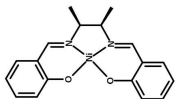
Table 1. continued

Monomer		Solvent	Substrate	Applications		Ref.
Monomer	Molecular formula	Molecular structure		Function	Device	
meso-N,N′-bis-(salicylidene)-2,3-butanediaminonickel(II)]	$C_{18}H_{18}N_2O_2Ni$	 	Propylene carbonate	Au film coated Ti underlayer	Electrodes	Pseudocapacitors	[26]

it is necessary to comprehensively consider the above factors to achieve the best capacitance performance. For instance, after compositing with conductive supporting materials, the capacitive properties of polymer materials would be improved greatly.

Meanwhile, except for the characteristic of monomers, the cost and weight of monomers should also be considered for potential commercialization. Among these monomers listed in tables, some commonly used monomers like pyrrole, pyrene, aniline and thiophene are cheap and commercially available. In addition, they have light weight (the density of pyrrole, pyrene, aniline and thiophene is 0.967 $g\,cm^{-3}$, 1.27 $g\,cm^{-3}$, 1.02 $g\,cm^{-3}$ and 1.05 $g\,cm^{-3}$, respectively) so that these monomers have great potential for practical energy devices. Other monomers such as 2,2-dimethylvinyl boric acid, 1,3,5-tris(N-carbazolyl)benzene and so on have complicated molecular structure and relatively high cost. They may be more suitable to be applied in constructing functional layer for electrodes because of the limited usage amount of monomers.

2.1.2. Substrates

In the synthesis process based on electropolymerization strategy, it is essential to use a suitable conductive substrate as the venue for initiating reaction, which should have the following key characteristics. Firstly, a substrate with good conductivity is the paramount condition to ensure efficient electropolymerization reaction. Patil et al. investigated the effect of substrate conductivity on the electropolymerization of poly(o-methoxyaniline) (POMA) by using the transparent conducting SnO_2 and SnO_2:F-coated glass substrates, respectively.[63] They found that the efficiency of the electropolymerization increased with the increasing conductivity of substrates. The surface morphology of the POMA films was also influenced by the substrate conductivity. Common conductive substrates include various carbon-based substrates,[40–42,44,48] metal substrates,[4,37,54] conductive oxide substrates,[17] and conductive glass substrates.[45,50] Secondly, the substrate should maintain good chemical stability under electropolymerization conditions, avoiding adverse reactions with the electrolyte or monomer. In addition, the substrate surface should have suitable hydrophilicity or hydrophobicity to allow uniform adsorption of the monomer on the substrate surface. For substrates with lower affinity, surface modifications can be applied to enhance substrate adhesion, ensuring firm attachment of the electropolymerized products. For instance, Marks et al. deposited a 200 nm layer of Indium tin oxide on fiber surfaces using magnetron sputtering to improve the affinity of the substratewith a biotinylated polypyrrole thin film.[64] Furthermore, selecting a substrate with sufficient mechanical strength and stability is essential to prevent deformation or damage during the electropolymerization process. The substrate should also has adequate thermal stability to resist potential temperature variations during electro-polymerization.

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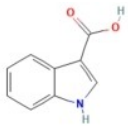
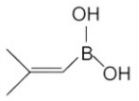
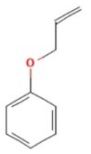
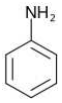
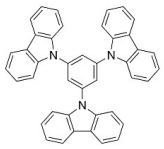
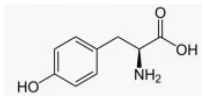
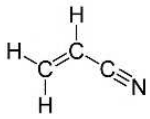
21960216, 2024, 12, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/celc.202300776 by Helmholtz-Zentrum Berlin Für, Wiley Online Library on [17/01/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 2. Monomers of electropolymerization for constructing electrode protective layers in batteries and supercapacitors.

Monomer			Solvent	Substrate	Applications		Ref.
Monomer	Molecular formula	Molecular structure			Function	Device	
Pyrrole	C_4H_5N		Ethylene carbonate/Diethyl carbonate/Ethyl Methyl Carbonate (EC/DEC/EMC)	Al foil	Cathode protective layer	LIBs	[21]
Thiophene	C_4H_4S		EC/DEC/EMC	Al foil	Cathode protective layer	LIBs	[20]
Indole-3-carboxylic acid	$C_9H_7NO_2$		EC/DEC	Al foil	Cathode protective layer	LIBs	[53]
2,2-dimethylvinyl boric acid	$C_4H_9BO_2$		EC/DEC	Copper foil	Anode protective layer	LIBs	[54]
Allyl phenyl ether	$C_9H_{10}O$		Dimethyl sulfoxide (DMSO)	Carbon nanotubes	Anode protective layer	LIBs	[55]
Aniline	$C_6H_5NH_2$		EC/DEC	Al foil	Cathode protective layer	Lithium-selenium batteries	[56]
Dipropyleneglycol dimethyl ether	$C_8H_{18}O$		1,2-Dimethoxyethane/1,3-Dioxolane (DME/DOL)	Al foil	Cathode and anode protective layer	LSBs	[57]
1,3,5-tris(N-carbazolyl)benzene	$C_{42}H_{27}N_3$		CH_3CN/CH_2Cl_2	Carbon nanotubes	Cathode protective layer	LSBs	[16]
L-tyrosine	$C_9H_{11}NO_3$		DME/DOL	Li metal	Anode protective layer	Lithium-metal batteries	[58]
Acrylonitrile	C_3H_3N		EC/DEC	Li metal	Anode protective layer	Lithium-metal batteries	[59]

2.1.3. Solvents

In addition to the monomer and substrate, solvent also plays a key role in the final products since electropolymerization typically takes place in a solution, which can be either organic solvents or water. When selecting a solvent, various factors need to be considered, including the monomer feature, matrix properties of the electrode, and experimental conditions. It is necessary for the solvent to be chemically stable during the electropolymerization to avoid adverse reactions with monomers or electrodes. Predominantly, the solvent should have sufficient conductivity to support the electropolymerization reaction. Improving the conductivity of the electrolyte can facilitate the electropolymerization reaction. Arbizzani et al.[65] electropolymerized poly(3-methylthiophene) in the 1-ethyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquid (IL) for the first time. An acid additive trifluoromethanesulfonimide (HTFSI) displaying the same anion of the IL was added, which provided an acid proton reduced to H_2 at the counter electrode and prevented consumption of IL during the electropolymerization process conferring a great advantage in terms of costs in comparison with traditional

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21960216, 2024, 12, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/celc.202300776 by Helmholtz-Zentrum Berlin Für, Wiley Online Library on [17/01/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

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Table 3. Monomers of electropolymerization for other functions in batteries and supercapacitors.

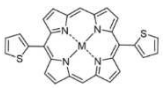
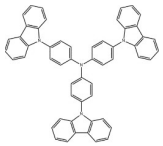
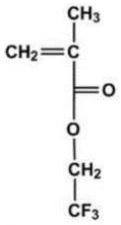
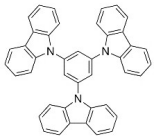
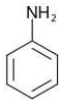
Monomer			Solvent	Substrate	Applications		Ref.
Monomer	Molecular formula	Molecular structure			Function	Device	
[5,15-di(thiophen-2-yl) porphinato] M(II)	C_4H_5N		Propylene carbonate/Fluoro-ethylene Carbonate (PC/FEC)	Al foil	Improving electrode stability	Organic batteries	[23]
4,4′,4″-Tris(carbazol-9-yl)-triphenylamine	$C_{54}H_{36}N_4$		EC/DEC	Al foil	Improving electrode stability	Organic batteries	[22]
Fluoroalkyl acrylate	$C_5H_7F_3O_2$		Solvent free	Al foil	Preparing interlayer	LIBs	[60]
1,3,5-tris(N-carbazolyl)benzene	$C_{42}H_{27}N_3$		CH_3CN/CH_2Cl_2	Indium tin oxide	Preparing interlayer	LSBs	[17]
Aniline	$C_6H_5NH_2$		Sulfuric acid solution	Cu foil	Modifying current collector	LIBs	[19]

Table 4. The capacitive properties of some polymer materials formed via electropolymerization.

Monomer	Polymers	Electrode system	Working electrode	Counter electrode	Reference electrode	Capacitance	Ref.
Pyrrole	Polypyrrole	Three-electrode	Graphite coated Ti	Pt coated Ti	Pt wire	535 $F g^{-1}$ at 20 $mV s^{-1}$	[42]
Pyrene	Polypyrene	Three-electrode	Carbon black coated PTEE	Active carbon sheet	Ag/AgCl	197 $F g^{-1}$ at 0.1 $A g^{-1}$	[43]
Aniline	Polyaniline	Three-electrode	Carbon cloth	Pt mesh	Ag/AgCl	115 $F g^{-1}$ at 5 $mV s^{-1}$	[61]
Oxometalates	Polyoxometalates	Three-electrode	Glassy carbon	Pt wire	Ag/AgCl	19 $F g^{-1}$ at 100 $mV s^{-1}$	[50]
Methylene blue	Poly(Methylene blue)	Three-electrode	Carbon fiber fabrics	Pt sheet	Ag/AgCl	89.67 $F g^{-1}$ at 0.3 $A g^{-1}$	[51]
3-methylthiophene	Poly(3-methylthiophene)	Three-electrode	Al sheet	Active carbon	Ag wire	170 $F g^{-1}$ at 5 $mV s^{-1}$	[62]
5-amino-2-naphthalenesulfonic acid	Poly(5-amino-2-naphthalene-sulfonic acid)	Three-electrode	Carbon cloth	Graphite rode	Saturated calomel electrode	40.4 $F g^{-1}$ at 1 $A g^{-1}$	[52]
2-heptadecyl-4,6-di-(thiophen-2-yl) thieno[3,4-d]thiazole	Poly(2-heptadecyl-4,6-di-(thiophen-2-yl) thieno[3,4-d]thiazole)	Three-electrode	Ti/Au coated quartz electrode	Pt wire	Ag/AgCl	224 uF cm^{-2} at 50 $mV s^{-1}$	[45]

electrolyte. Zou et al. used a new type of ionic liquids (ILs) as solvents, e.g. novel proton-functionalized solid anilinium salts (anilinium nitrate ([HANI]NO_3) and anilinium hydrochloride ([HANI]Cl)) with glycol in appropriate ratios.[66] This IL-based solvent has higher conductivity and lower viscosity, making it suitable for electropolymerization. Compared to acidic aqueous

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solutions, the electropolymerization efficiency is significantly improved in IL-based solvent. Similarly, Abad-Gil et al. developed for the first time binary (choline chloride and ethylene glycol) and ternary (choline chloride, ethylene glycol and fructose) deep eutectic solvent (DES) mixtures based on choline chloride and applied it as media for the electropolymerization of poly(methylene blue) (PMB) on glassy carbon electrodes.[67] Adding counter ions would affect the oxidation potential of electropolymerization, the morphology and conductivity of the polymer products. Aubert et al.[68] investigated the influence of counter ions (ClO_4^-, BF_4^-, PF_6^-,$CF_3SO_3^-$) to the electropolymerizaiton of 3,4-Ethylenedioxythiophene (EDT) and thieno-(3,4-b)-2,3-dihydro-2-tetradecyl-1,4-dioxane (EDT-C14) respectively. As a result, PEDT and PEDT-C14 tended to lower monomer oxidative potentials during electropolymerization by a negative shift up to 250 mV in case of PF_6^- and ClO_4^-. Meanwhile, the highest conductivities of polymer products were obtained with ClO_4^- and BF_4^- as counter ions.

In some cases, the addition of surfactants or stabilizers as auxiliary agents can improve the effectiveness of electropolymerization. Castro-Beltran et al. separately added anionic additives dioctyl sodium sulfosuccinate (AOT) and polymeric additives poly(diallyldimethylammonium chloride) (PDADMAC) to the solvent.[69] They found that anionic additives promote the oxidation of the monomer and increase the polymerization rate, while polymeric additives enhance the adhesion of the electrodeposited polypyrrole (PPy) film. Li et al. added nonionic surfactants nonaphenol polyethyleneoxy (n) ether (OP_n, where n = 4, 7, 10, 15, or 21) to the solvent.[70] Compared to solutions without additives, the mechanical properties and surface smoothness of the polypyrrole (PPy) films are greatly improved. The addition of an appropriate amount of soft template molecules to the solvent can effectively control the morphology of the electropolymerization product. Yu et al. added 0.1 M of the soft template molecule p-toluene sulfonic acid (TsOH) to the solvent during the electropolymerization of polypyrrole (PPy).[5] PPy nanowires was successfully achieved on a non-precious nickel foam substrate. It is found that Ts^+ ions can dope into the initially formed PPy oligomers. The π-π interaction between the pyrrole in PPy oligomers and the aromatic rings of TsOH results in electrostatic adsorption, promoting the subsequent formation and growth of PPy nanowires at the tips of nuclei. Additionally, solvent can also influence the morphology of the electropolymerization product. Poverenov et al. investigated the influence of solvents, namely propylene carbonate (PC) and acetonitrile (MeCN), on the morphology of electropolymerized poly(3,4-ethylenedioxythiophene) (PEDOT). They found that the solubility of short 3,4-ethylenedioxythiophene (EDOT) oligomers in PC was three times higher than that in MeCN. This resulted in PEDOT exhibiting a smooth and flat morphology in PC, while displaying a bumpy star-shaped pattern in MeCN.[38] It's worth noting that during in situ electropolymerization inside the battery, the battery electrolyte is often directly used as the solvent. This not only diversifies the types of electropolymerization solvents but also conserves the use of additional solvents.

2.1.4. Voltage

Externally applied voltage and current or temperature are also crucial factors influencing the progressing of electropolymerization. During the electropolymerization, only when reaching a critical voltage value can the monomer be oxidized and polymerized. In different electropolymerization systems, the required minimum critical voltage varies. This value can be determined through the oxidation potential obtained from Cyclic Voltammetry (CV) tests. During electropolymerization, if the applied voltage exceeds a certain value, the solvent can undergo oxidation and decomposition. Therefore, the applied voltage should be kept below the decomposition voltage of the solvent. Hu et al. studied the voltage upper limit of the mixed solutions with different volume ratios of water to acetonitrile of 2:1, 1:1, and 1:4.[71] They found that as the water content decreased, the stable voltage of the solvent increased. Within a reasonable voltage range, voltage influences the electropolymerization rate. For instance, Wood et al. investigated the relationship between film mass and time during the electropolymerization of PPy on carbon fibers under different applied voltages.[72] They found that, at the same time, film mass significantly increased with increasing voltage. Voltage also has an impact on the morphology and performance of the electropolymerization product. Cysewska et al. investigated the influence of voltage on the morphology and conductivity of electropolymerized PEDOT films with Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode.[39] They found that the PEDOT films exhibited the maximum area at a synthesis voltage of 1.2 V and reached the minimum at 1.4 V. Correspondingly, the double layer capacitance also decreased from 2.3 mF to 1.5 mF. Wang et al. investigated the influence of voltage on the morphology of electropolymerized donor-acceptor-donor (D-A-D) type monomers.[73] They found that as the voltage increased, the color of the electropolymerization product changed gradually from light yellow to deep blue. For the electropolymerization of mixed monomers, voltage could also affect the composition of the product. Xu et al. found that during the electropolymerization of polypyrrole-dodecylbenzenesulfonate (PPy(DBS)), the product exhibited higher sulfur content and lower nitrogen content at high voltage.[74] In addition, temperature also influences the morphology of electropolymerization products. Luo et al. investigated the impact of temperature on the morphology of electropolymerized poly(hydroxymethyl 3,4-ethylenedioxythiophene) (poly(EDOT–OH)).[75] They found that poly(EDOT–OH) formed nanodots during electropolymerization at 25 °C, while it formed tubular nanostructures when electropolymerization occurred at 0 °C. Meanwhile, at lower temperatures, the growth rate of the product also decreased.

2.2. Morphology

The morphology of electropolymerization products is influenced by factors such as monomers, substrates, solvents, and voltage. Subsequently, morphology further affects the electro-

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chemical performance of batteries and supercapacitors. The first characteristic result derived from electropolymerization is a spatial morphology with high specific surface area, which significantly optimizes the electrochemical reaction interface and site to improve the electrochemical performance of the device. Xu et al.[44] used a one-step electropolymerization method to synthesize nitroxide free radical-containing polypyrrole copolymer, which is served as an organic electrode material. The copolymer displayed an open porous structure while polypyrrole (PPy) exhibited an aggregated morphology. The open porous structure confers a large specific surface area and a quick lithium ion diffusion. As a result, the initial discharge capacity was greatly improved from 41.0 mAh g^{-1} to 70.9 mAh g^{-1} in comparison with pure PPy. Zhang et al.[19] conducted electropolymerization of polyaniline (PANI) on copper foil to create a novel composite current collector, PANI/Cu. The PANI layer increased the contact area between the current collector and the active material, thereby enhancing the properties. The second typical feature is that when electropolymerization products are used as electrode protective layers, their morphology tends to be thin layer structure, which could wrap the active materials closely and would not block the lithium ion diffusion. Dong et al.[20] conducted an in situ electropolymerization on the NCM811 surface to form an elastic conductive polythiophene (PTh) layer with a thickness of around 4 nm. This thin PTh layer stabilized the electrode interface, prevented electrolyte corrosion, and reduced charge transfer resistance.

Hierarchical systems for electrode with multiple functions to achieve high energy storage performance is another important characteristic induced by morphology regulation in electropolymerization. On one hand, conducting polymers can be active materials or serve as a template for the loading of active materials due to their ease of functionalization. On the other hand, nanostructured conducting polymers usually have large surface area that is conducive to the quick diffusion of electrolytes, the release of the performance of electrodes, and the buffer of the volume expansion. Furthermore, a continuous conducting framework can be kept after the loading of active materials. To construct a hierarchical system, the electropolymerization of conducting polymers on a porous substrate is a crucial step. Carbon materials are usually good choice to work as nucleation sites due to the strong interactions between polymer molecules and carbon substrates. But for metal substrates like nickel foam, a noble metal (e.g. Au, Pt, and Pd) is often needed as the nucleation sites for electropolymerization of conducting polymers on substates. Yu et al.[5] introduced an appropriate amount of p-toluenesulfonic acid into electrolyte to enhance the nucleation of conducting polymer in the electropolymerization of polypyrrole (PPy) and fabricated MoS_3@PPy nanowires on porous nickel foam via e electrodeposition. In this hierarchical system, nickel foam works as framework of self-standing electrode while PPy nanowires work as loading place for MoS_3 nanoparticles, which makes a much more uniform distribution of MoS_3 nanoparticles and a fast lithium ion diffusion. Sun et al.[41] spray coated poly(vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibers on the cotton fabric (CF) and naturally dried in air to form a flexible textile substrate, and then electropolymerized sea urchinspines-like PPy arrays on the composite substrate, which can work as electrodes with hierarchical structure for supercapacitors. In this hierarchical system, cotton fabric (CF) is employed as the raw substrate with an excellent flexibility and interconnected porous structure. The PVA-co-PE nanofibers with abundant hydrophilic hydroxyls groups make a good adhesion between cotton fabric and polypyrrole arrays. Itoi et al.[43] used a gas-phase method to introduce pyrene and aniline (ANI) separately into the pores of activated carbon (AC) and conducted an in situ electropolymerization to form pseudocapacitive polypyrene and polyaniline (PANI). In this hierarchical system, AC works as a highly conductive media and provides rich double-layer capacity while polypyrene or PANI offers certain pseudocapacity, greatly enhancing the total capacity of the electrode. In short, Table 5 lists the morphology and corresponding electrochemical properties of representative electropolymerization products in energy storage devices.

2.3. Characterization

Characterizing the polymer obtained from electropolymerization is a crucial step to understand its structure, properties, and performance. In addition to conventional characterization methods for polymers, such as Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Thermal Analysis Techniques (e.g. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)), etc., there are some commonly used unique methods for electropolymerization. For instance, Cyclic Voltammetry (CV) is employed to determine the redox potentials of monomers in the system, aiding in the selection of appropriate voltage ranges for electropolymerization.[66,76] It can also observe the reversibility and stability of the electropolymerization process, determining the limits of the reaction. Current-time curves (IT) characterize the speed and difficulty of the electropolymerization reaction.[69] The conductivity of electropolymerization products is a critical parameter, often characterized by impedance spectroscopy.[39] UV-Vis absorption spectroscopy is used to characterize the impact of polymer films on light transmittance, providing clarity on the formation of polymer films.[63,66] Fourier transform infrared spectroscopy (FTIR) and Nuclear magnetic resonance (NMR) are often used to observe changes in the molecular structure of organic compounds before and after electropolymerization, determining product composition and structure.[69,77] Atomic force microscopy (AFM) is frequently used to observe and characterize the thickness of the polymer films.[38,76] Occasionally, to observe the strength of the bond between electropolymerization products and substrates, adhesion tests can be conducted.[69]

Additionally, there are some methods with specific requirements, such as cryo-transmission electron microscopy[78] (Cryo-EM) and Time of flight secondary ion mass spectrometry (ToF-SIMS).[79,80] Some electropolymerization products, such as solid electrolyte interface (SEI) membranes, undergo significant

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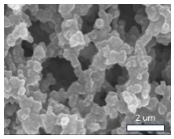
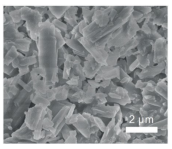
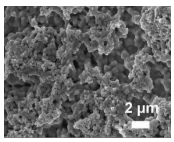
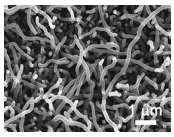
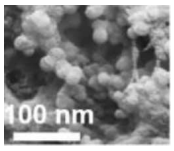
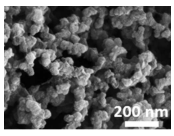
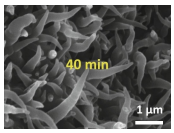
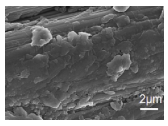
21960216, 2024, 12, Downloaded from https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/celc.202300776 by Helmholtz-Zentrum Berlin Für, Wiley Online Library on [17/01/2025]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Table 5. The morphology of some electropolymerization products and their corresponding device properties.

Monomer	Morphology of polymers	Morphology characteristic	Device	Property	Ref.
Nitroxide free radical-contained pyrrole		Open porous structure	Organic batteries	70.9 mAh g^{-1} at 20 mA g^{-1}; after 20 cycles, 24.4% loss of capacity	[44]
4,4′,4′′-Tris(carbazol-9-yl)-triphenylamine		Uniform crystals	Organic batteries	92 mAh g^{-1} at 0.1 Ag^{-1}; after 5000 cycles, 48 mAh g^{-1} remained at 1 Ag^{-1}	[22]
4-(thiophene-3-yl) benzenethiol		Loose granular structure	LSBs	870 mAh g^{-1} at 0.1 C; after 100 cycles, 600 mAh g^{-1} remained at 0.2 C	[4]
Pyrrole		Uniformly distributed nanowires	LSBs	730 mAh g^{-1} at 0.09 Ag^{-1}; after 100 cycles, 540 mAh g^{-1} retained at 0.45 Ag^{-1}	[5]
1,5-naphthalenedi-amine		Homogeneously distributed spherical particles	Aqueous ZIBs	129 mAh g^{-1} at 0.05 Ag^{-1}; after 1000 cycles at 5 Ag^{-1}, a retention of approximately 100%	[37]
2,6-naphthalenedi-amine		Irregular particles	Aqueous ZIBs	133.1 mAh g^{-1} at 0.05 Ag^{-1}; after 8000 cycles at 1 A g^{-1}, 44.6 mAh g^{-1} remained	[49]
Pyrrole		Prominent horn shape	Pseudocapacitors	918.74 mF cm^{-2} at 0.4 mA cm^{-2}; after 10000 cycles, the retention reached 95.3%	[41]
5-amino-2-naphthalenesulfonic acid		Particle-like structure	Pseudocapacitors	85.5 mAh g^{-1} at 1 Ag^{-1}; 88% capacitance retention after 10000 cycles at 5 A g^{-1}	[52]

morphological changes when subjected to high-voltage electron bombardment in conventional electron microscopy, making it difficult to observe the true morphology of organic thin films. The development of cryo-electron microscopy has effectively addressed this issue. Zeng et al. in situ electropolymerized an polydopamine (PDA) solid electrolyte interface on the zinc anode (Figure 2a), and used focused ion beam scanning electron spectrometry (FIB-SEM) (Figure 2b) and cryo-electron microscopy (Cryo-EM) (Figure 2c–d) to visually observe the morphology of the solid electrolyte interface.[78] Sometime, the electropolymerization products are extremely thin of only tens of nanometers, which is challenging to be detected by conventional characterization methods. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a highly sensitive surface analysis technique that can precisely characterize the composition of organic thin films. Varol et al. in situ electropolymerized polydopamine (PDA) film on the surface of a porous substrate (Figure 2e) and used ToF-SIMS to monitor the variation trend of CN^- content with the number of electropolymerization cycles (Figure 2f–h).[79] Gu et al. used ToF-SIMS to characterize the composition and element distribution of the solid electrolyte interface formed by in situ electropolymerization on the graphite anode.[80]

In this section, we have introduced the main components of electropolymerization, including monomers, solvents, substrates, and applied voltage and current. We have compiled a list of electropolymerization monomers used in recent years for batteries and supercapacitors. Additionally, we have empha-

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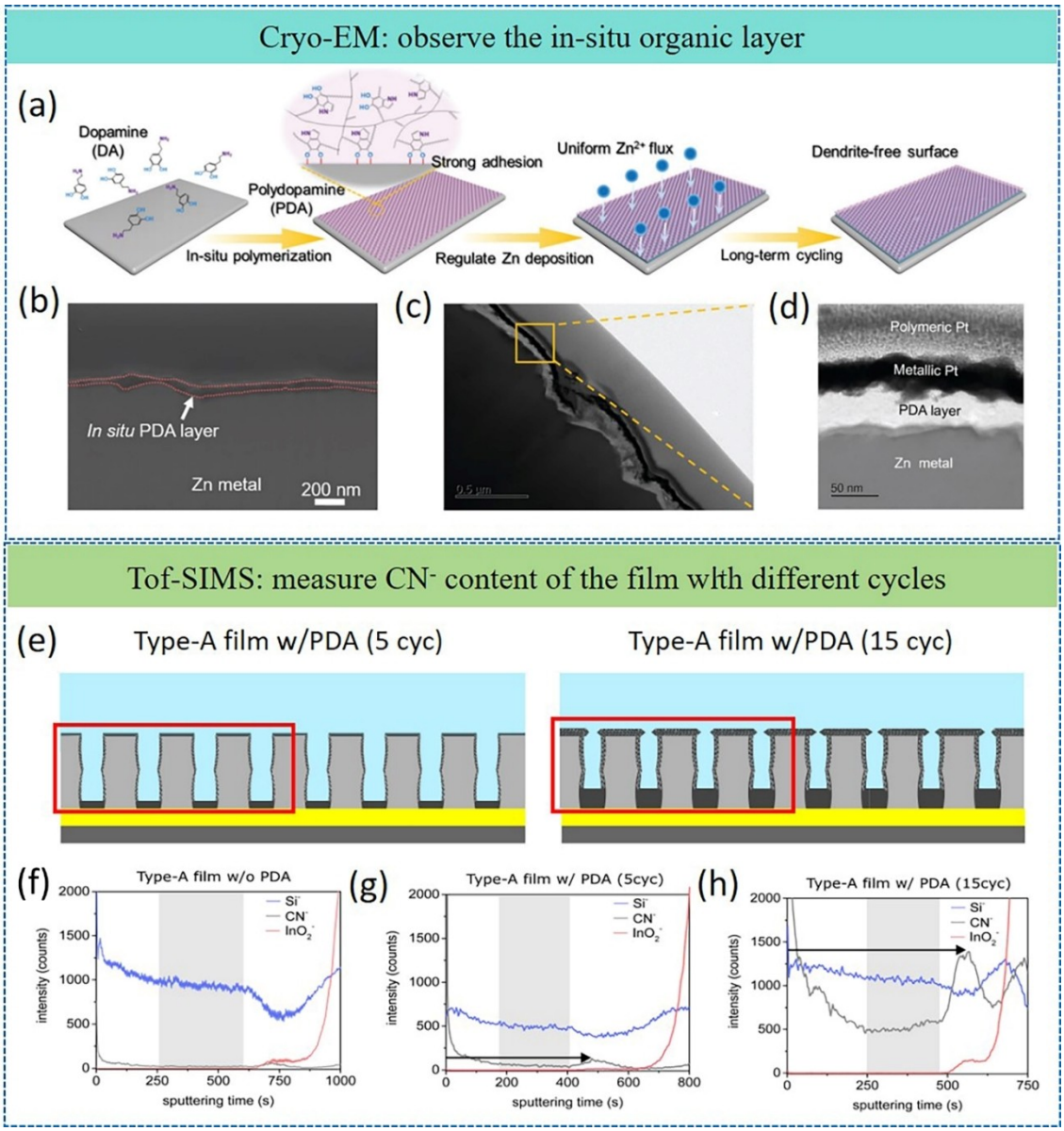

Figure 2. (a) Schematic illustration of the in situ formation of the multifunctional PDA solid electrolyte interface; (b) Side-view focused ion beam (FIB)-SEM images of the Zn electrode after 10 cycles in the electrolyte with dopamine; (c) Low-resolution and (d) high-resolution cryo-transmission electron microscopy (cryo-EM) images of the Zn electrode with the polydopamine (PDA) layer; Reproduced with permission.[78] Copyright 2021, The Royal Society of Chemistry. (e) Illustrations of mesoporous films after their PDA functionalization with 5 and 15 cycles; Time of flight secondary ion mass spectrometry (ToF-SIMS) depth profiling data of (f) pristine (no PDA), and PDA-functionalized films after (g) 5 and (h) 15 electropolymerization cycles. Reproduced with permission.[79] Copyright 2023, American Chemical Society.

sized how to select solvents and substrates. Improving the conductivity of substrates and solvents, enhancing substrate affinity, and adding additives to the solvent can improve the efficiency and quality of electropolymerization. Monomers and solvents are the primary factors influencing the morphology and properties of electropolymerization products. Furthermore, we have introduced common characterization methods used in the electropolymerization process and for electropolymerization products, as well as some specialized characterization techniques. Through this content, we believe it can provide guidance and reference for the preparation and characterization of electropolymerization.

3. Application in Batteries and Supercapacitors

Electropolymerization finds extensive applications in various energy storage devices, including organic batteries, LIBs, LSBs, ZIBs, and supercapacitors. Its applications encompass the preparation of organic electrodes, construction of protective layers, design of intermediary layers and so on. This chapter focuses on the batteries and supercapacitors applications reported in recent years based on electropolymerization strategies, as well as the electrochemical properties and mechanisms related to electropolymerization.

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3.1. As organic electrodes

The most significant advantage of electropolymerization in the preparation of organic electrodes lies on the fabrication of self-supporting electrodes. Compared to other methods, this not only reduces the use of non-active materials in the electrode but also results in a better integration between the electrode material and the current collector, enhancing electrochemical efficiency. Additionally, due to the tunability of the molecular structure of organic compounds, a wide variety of organic electrodes can be obtained. This application has been widely implemented, particularly in organic batteries, zinc batteries, Li–S batteries, and supercapacitors.

Organic electrode materials, characterized by the presence of abundant elements (e.g., carbon, hydrogen, and oxygen) have become a research hotspot in next-generation battery systems in recent years because of their renewable, environmentally friendly, low cost, high capacity, and other advantages. However, organic electrode materials still face challenges such as high solubility in electrolytes, poor conductivity, and low density. Friebe et al.[48] modified conductive polythiophene with (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) units and prepared an organic free-standing electrode by electropolymerization. No additional conductive agents and binders are required. Quantum chemical simulations clearly revealed that during the charging process, oxidation occurs first on TEMPO, followed by reversible oxidation of the oligothiophene at higher voltages. The initial discharge specific capacity of the electrode was 30 $mAh \cdot g^{-1}$, corresponding to 50% of the theoretical capacity. The electrode exhibited excellent cycling performance, with a small capacity decay rate of only 0.03% after 3000 cycles. The organic electrodes prepared by electropolymerization allow for a better interface between the active material and the current collector. Xu et al.[44] used a one-step electropolymerization method to synthesize nitroxide free radical-containing pyrrole copolymer (PPy-co-Ppy-C-TEMPO) as an organic electrode material. PPy-co-Ppy-C-TEMPO consists of numerous interconnected small particles of approximately 400 nm, forming a regular star-shaped structure. The specific capacity of PPy-co-PPy–C-TEMPO (4:1) and PPy-co-Ppy-C-TEMPO (8:1) are 70.9 $mAh\,g^{-1}$ and 62.6 $mAh\,g^{-1}$ at 20 $mA\,g^{-1}$ between 2.5 and 4.2 V, respectively. Compared with the value (41.0 $mAh\,g^{-1}$) of the PPy cathode measured under the same condition, capacity of the composite cathode was greatly improved. The introduction of TEMPO enhanced the specific surface area of the composite electrode, facilitating the utilization of the active material and thereby improving electrochemical performance. Compared to LIBs, organic batteries based on electropolymerization often exhibit low capacity but long cycle life. Fullerene has high conductivity and its surface has high reaction activity that can graft various organic functional group to form composite monomer.[81] For battery electrodes based on pure organic polymers, the introduction of conductive fullerene can greatly improve the utilization efficiency of electrodes.[82] Chen et al.[27] electropolymerized a fullerene-functionalized terthiophene monomer, N-methyl-2-(2-[2,2′;5′,2″-terthiophen-3′-yl]ethenyl)fullero [3,4]pyrrolidine (TTh-BB) to form the homopolymer P(TTh-BB) as the electrode of organic battery. In comparison with the electrode without functional fullerene group, the discharge capacity of P(TTh-BB) attained a near 1.5 times improvement. Meanwhile, the cycle performance has also increased by 2.5 times. In future development, there is an urgent need to explore and develop more organic batteries with higher capacity to broaden their application scope.

Zinc batteries including zinc-ion batteries (ZIBs) and zinc-air batteries are known for their high energy density, rapid charge and discharge rates, and cost-effectiveness, making them widely used in energy storage systems. Meng et al.[40] employed electropolymerization to coat heavily N-doped carbon on the surface of the single-walled carbon nanotubes (SWCNTs), creating an N/CSWCNT composite electrode (Figure 3a). TEM images of the PPy-SWCNTs (Figure 3b) showed that a ~12 nm-thick PPy layer was uniformly coated on the SWCNT bundles. This composite electrode is rich in pyridinic N, which provides excellent catalytic activity for both the evolution reactions and oxygen reduction. When this composite electrode was used as the oxygen electrode in zinc-ion batteries, the battery demonstrated impressive performance with a high peak power density of 181 $mW\,cm^{-2}$, a high specific capacity of 810 $mAh\,g^{-1}$, and a long cycling life. Pan et al.[37] used 1,5-naphthalenediamine (1,5-NAPD) monomers for the cathode in ZIBs, which directly electro-polymerized into poly(1,5-NAPD) during the initial oxidation process. This electrode exhibited an initial capacity of 129.4 $mAh\,g^{-1}$ at 0.05 $A\,g^{-1}$ and demonstrated excellent cycling stability, with no significant capacity decay observed even after 1000 cycles. The authors proposed a possible mechanism for the polymerization of 1,5-NAPD monomers into poly(1,5-NAPD), which contains three stages during the polymerization process. Initially, free radicals with a positive charge generates in the 1,5-NAPD monomers as electrons are driven away from the amine groups under the electric field. Subsequently, these free radicals rearrange and combine to form dimer free radicals. Finally, dimer free radicals grow gradually and form a long polymer chain. Similarly, Xie et al.[49] used 2,6-naphthalenediamine (2,6-NAPD) monomers as the electrode material for ZIBs, which demonstrated a specific capacity of 133.1 mA h g^{-1} at 0.05 $A\,g^{-1}$ and exhibited excellent cycling stability, retaining 76.5% of its initial capacity after 8000 cycles. The authors also proposed a possible electro-polymerization pathway for 2,6-NAPD monomers. Firstly, the 2,6-NAPD monomer transfers to form naphthol by combining with two hydroxide ions in a $ZnSO_4$ solution. Subsequently, naphthol is converted to naphthylamine with the pH value changing in the electrolytes. Secondly, free radicals with a positive charge generates since electrons are driven away from the amine groups of the 2,6-NAPD monomer. This free radical creates an active radical via electronic rearrangement near the amine group in naphthoquinone. Subsequently, two free radicals combine into a dimer free radical through N-H bonding. Finally, dimer free radicals grow gradually and form a long polymer chain

Li–S batteries (LSBs), with a theoretical specific capacity of up to 1675$mAhg^{-1}$ and a theoretical energy density of 2600$Whkg^{-1}$, as well as the low cost and environmental friendliness of sulfur, hold the potential to replace LIBs as the

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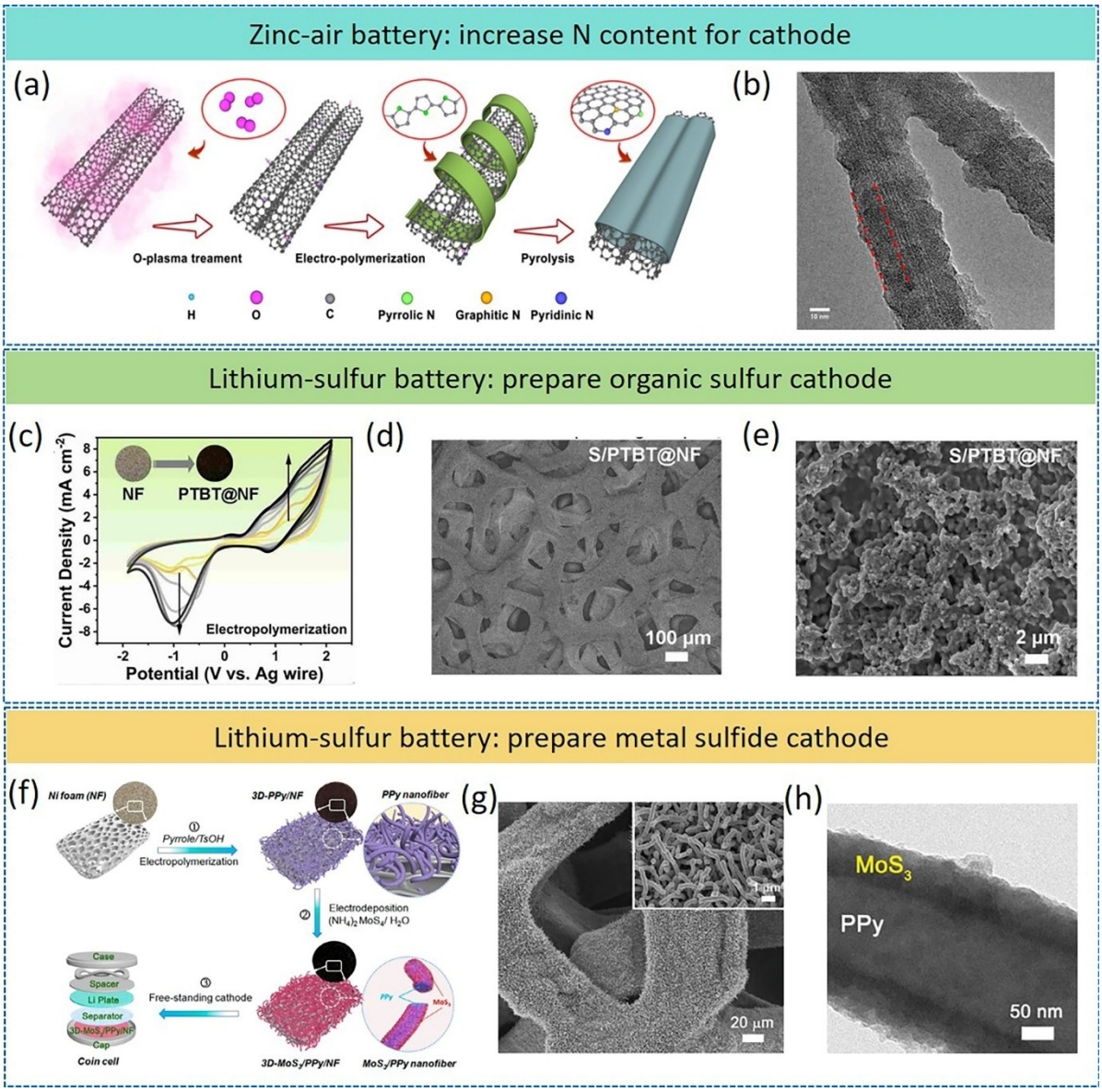

Figure 3. (a) Schematic showing preparation of the core/shell structured N/C-(Single-walled carbon nanotube)SWCNT film; (b) High-resolution TEM image of the PPy-SWCNTs (The PPy coating is between the dashed red lines); Reproduced with permission.[40] Copyright 2023, Nature. (c) Repeated potential scan electro-polymerization of 4-(thiophene-3-yl) benzenethiol (TBT) in 0.1 m TBAPF6/ACN at 100 mVs; SEM images of S/(Poly(4-(thiophene-3-yl) benzenethiol))-@Nickel Foam(S/PTBT@NF) with (d) low and (e) high magnification; Reproduced with permission.[4] Copyright 2022, Wiley-VCH GmbH. (f) Fabrication route of the sulfur-equivalent MoS_3/PPy/NF cathode through electrochemical methods; (g) SEM and (h) TEM images of MoS_3/PPy/NF cathode. Reproduced with permission.[5] Copyright 2022, John Wiley & Sons Australia.

next generation of commercial batteries.[83,84] However, shuttle effect remains a persistent issue for LSBs.[85] In contrast to elemental sulfur, sulfur in organic compounds often exists in the form of short chains, preventing the formation of high-order polysulfides and thereby eliminating the shuttle effect.[86,87] Ning et. al.[4] prepared an organic sulfur electrode based on the thiol-containing conducting polymer poly(4-(thiophene-3-yl) benzenethiol) (PTBT) by electropolymerization (Figure 3c). Figure 3d exhibits the nickel wires are uniformly coverd by PTBT, but there are many pores in PTBT film (Figure 3e). The main chain in polythiophene-structure serves as the conductive framework, while the side chain in the benzenethiol forms covalently linked organic sulfur polymers (S/PTBT). The organic sulfur electrode exhibited a reversible capacity of around 870 mAh g^{-1} at 0.1 C. When S/PTBT is immersed in CS_2 and compared to the physically mixed cathode (S&PTBT), there is no sulfur appears, indicating the cycling performance was significantly improved. The remarkable effect of suppressing the shuttle of polysulfides through the introduction of covalent bonds has been further proved by operando X-ray imaging results. In addition to elemental sulfur and organic sulfur, metal sulfides also serve as excellent cathode active materials for LSBs. Compared to elemental sulfur, metal sulfides exhibit high conductivity, excellent reaction kinetics, lower

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volume expansion, and a wide range of material choices. Based on these advantages, MoS_3@PPy nanowires were fabricated on porous nickel foam via electrodeposition, resulting in a composite MoS_3/PPy/NF electrode (Figure 3f).[5] SEM images demonstrate that MoS_3@PPy nanowires are densely and uniformly distributed on the nickel foam, tightly wrapping around it (Figure 3g). TEM images show that the PPy nanowires are uniformly coated with MoS_3 nanoparticles with a thickness of about 50 nm (Figure 3h). MoS_3 possesses a unique electrochemical mechanism, preventing the generation of high-order polysulfides during discharge and eliminating shuttle effects, which further improves the cycling performance of the battery.

Supercapacitors are electronic devices that mainly store and release charge on the surface of electrodes. They are known for their extremely fast charge and discharge rates, as well as their long cycling lifetimes. However, standalone double-layer supercapacitors often have a relatively small energy storage capacity.[88] In comparison to double-layer capacitance, pseudocapacitive behavior involves certain electrochemical reactions and higher capacity. Conducting polymers, such as polyaniline, polypyrrole, and polythiophene, exhibit pseudocapacitive behavior.[89] The pseudocapacitance of conducting polymers mainly arises from the reversible oxidation and reduction of π-conjugated double bonds in polymer networks. The use of electropolymerization allows for the convenient preparation of self-supported supercapacitor electrodes based on conducting polymers on conductive substrates. This imparts the electrode with both double-layer capacitance and pseudocapacitance behavior. Alshehri et al.[50] prepared Lindqvist-type polyoxometalates (POMs) through the co-electropolymerization of $[Mo_6O_{18}NPhPy]^{2-}$, $[Mo_6O_{18}NPhCCPhPy]^{2-}$, and pyrrole. By introducing a substantial faradaic contribution through the POM redox processes, the electrochemical performance of the polypyrrole (PPy) film was improved with significantly reduced charge-transfer resistance of the films and enhanced specific capacitance.

In supercapacitors, various porous materials, such as cotton fabric, carbon fiber, carbon cloths, and nickel foam, are often used as substrates. Choi et al.[45] electro-polymerized 2-heptadecyl-4,6-di(thiophen-2-yl)thieno[3,4-d]thiazole (HDTTT) on several substrates including carbon, gold, platinum, and fluorine-doped tin oxide. HDTTT, which contains thiophene functional groups, was observed to show a distinct capacitive behavior. Sun et al.[41] used a flexible substrate consisting of cotton fabric (CF) coated with Poly (vinyl alcohol-co-ethylene) (PVA-co-PE) nanofibers (NF) to create a structure on which they built spines-like PPy arrays. These spiny PPy arrays serve to reduce the transmission path length for counter ions and charges, thus mitigating stress-induced damage to the PPy skeleton. Importantly, the flexible solid-state symmetrical supercapacitor (EPPy-PPy/NF/CF) demonstrates remarkable cycling stability, maintaining 100% of its initial capacity after 10,000 cycles at 4 mA cm^{-2}. Ozdemir et al.[42] electro-polymerized PPy on graphite to create a composite electrode. They used a deep eutectic solvent mixture of urea and choline chloride as the deposition solution. The capacitance behavior of the composite electrode was tested using different electrolytes, including water containing $LiClO_4$, acetonitrile containing $LiClO_4$, and pure Reline. The results showed that PPy displayed capacitance behavior in all these cycling electrolytes. In both aqueous and organic electrolytes, the PPy/graphite composite electrode reached a capacitance of 535 F $g^{-1}$with good cycling stability.

Conducting polymer hydrogels (CPH) and coordination polymers can also be applied as electrodes for supercapacitors. The high flexibility, continuous interconnected structure, and high electron/ion transfer efficiency of CPH confer it a great potential in fabrication of flexible solid-state supercapacitors. Chu et al.[24] fabricated a three-dimensional conducting polymer hydrogel (CPH) free of frameworks and initiators via electropolymerization of aniline and phytic acid. This CPH possesses a high conductivity and improved electrode interfaces between electronic transporting phase and ionic transporting phase. As a result, the CPH exhibit large areal capacitance of 561.6 mF cm^{-2} and specific capacitance of 311.3 F g^{-1}. After running 10000 cycles, it reaches a high 76% capacitance retention. The electrodes consisted of traditional conducting polymers have a relatively low voltage leading to low energy density. To solve this problem, Lepicka et al.[26] prepared a redox conductive coordination polymer film, poly[meso-Ni(II)-SaldMe], as the electrode of an asymmetric supercapacitor via the electropolymerization of a meso-N,N′-bis-(salicylidene)-2,3-butanediaminonickel(II)] monomer, meso-Ni(II)-SaldMe. The metal ions in coordination polymers could bring high voltage for electrodes. This coordination polymer-based supercapacitor has a wide voltage range of 0 to 2.2 V and exhibits a high energy density of 102.6 Wh kg^{-1} at the power density of 12.21 kW kg^{-1}.

3.2. As protective layer for electrode

In batteries, especially in LIBs and LSBs, the design of electrode protective layers based on the principle of electropolymerization has found widespread applications. Compared to other methods, electropolymerization enables the construction of protective layers between the active materials inside the electrode, achieving in situ protection. Additionally, due to the tunability of the molecular structure of organic compounds, protective layers with various functionalities can be designed.

LIBs are currently the most commercially mature rechargeable batteries widely used in mobile phones, laptops, new energy vehicles, energy storage stations, and more. In LIBs, the cathode active materials are often based on inorganic layered oxides[90–92] and olivine-type phosphates.[93–95] Electropolymerization in the LIBs system is often applied by exerting influence through the electrolyte on the electrode. $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) is a promising material of LIBs cathode. However, it is prone to corrosion by the electrolyte, leading to an unstable electrode interface and electrode structure collapse. Dong et al.[20] have added thiophene to the electrolyte, which underwent in situ electropolymerization on the NCM811 surface to form an elastic conductive polythiophene (PTh) layer (Figure 4a). TEM image of the NCM811@PTh-0.2% shows the thickness of the PTh protective layer is around 4 nm (Figure 4b).

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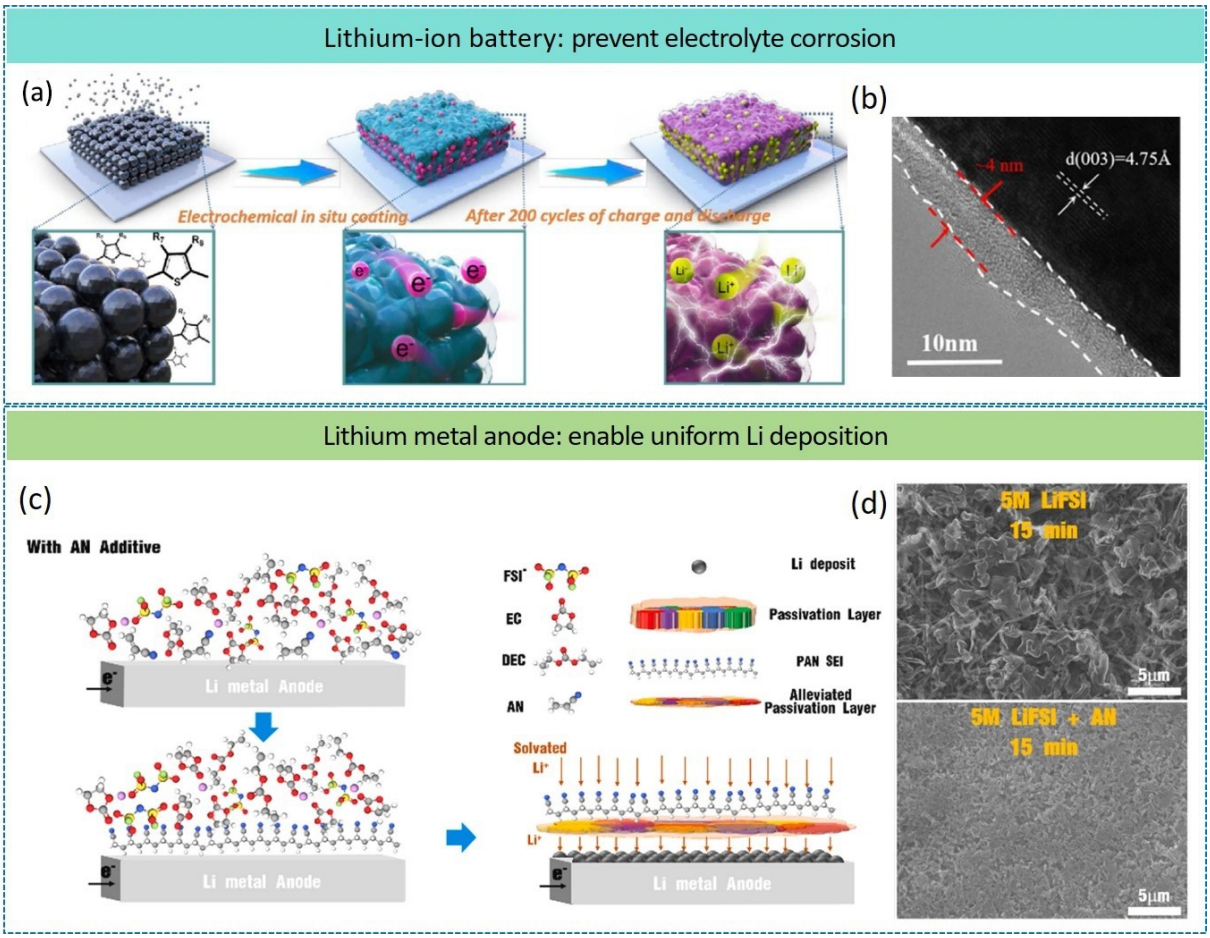

Figure 4. (a) The schematic illustration of in situ electrochemical polymerization of polythiophene (PTh) on NCM811 and stabilization of structural integrity; (b) Typical HRTEM image of the NCM811@PTh-0.2 %; Reproduced with permission.[20] Copyright 2023, Elsevier. (c) The mechanism of uniform Li deposition enabled by the polyacrylonitrile (PAN)-SEI from in situ electropolymerization of acrylonitrile (AN) additive; (d) Top-view SEM images of galvanostatic (1 mA cm^{-2}) Li deposition in 5 M LiFSI electrolyte without and with AN additive after 15 min. Reproduced with permission.[59] Copyright 2021, Elsevier.

This PTh layer stabilized the electrode interface and prevented electrolyte corrosion. Additionally, the PTh layer reduced charge transfer resistance and improved lithium-ion diffusion efficiency. As expected, the NCM811 modified with PTh demonstrated a significant rate capability with a high specific capacity of 171.7 mAh g^{-1} at 5 C and an enhanced cycling stability with 94 % capacity retention after 200 cycles at 2 C. This study demonstrates that using conductive polymer as an elastic layer is an effective and feasible approach to protective electrode materials. Similarly, Nie et al.[21] prepared a conductive (PPy layer on the surface of NCM811 by in situ electropolymerization to stabilize the electrode interface. Anothumakkool et al.[53] achieved in situ encapsulation of indole-3-carboxylic acid (InAc) on the surface of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) cathode through electropolymerization. InAc releases protons (H^+) in situ after oxidation. These protons (H^+) contribute to the formation of the cathode electrolyte interface and solid electrolyte interface at the surfaces of the cathode and anode, respectively. This reduces lithium-ion consumption and enhances the Coulombic efficiency of the battery.

Anode is also a crucial component in batteries. For LIBs, apart from graphite, materials like carbon nanotubes, hard carbon, and silicon,[96,97] etc., are promising alternative electrode materials. Yu et al.[54] utilized 2,2-dimethylvinyl boric acid (DEBA) to modify the surface of hard carbon (HC), resulting in the HC-DEBA composite material used as battery anode. During cycling, the C=C bonds of DEBA molecules undergo in situ polymerization on the hard carbon surface, forming a polymer inert protective layer. This layer prevents the corrosion and degradation of hard carbon from the electrolyte. In ester-based electrolyte, the initial Coulombic efficiency of the optimized HC-DEBA-3 % increases from 65.2 % to 77.2 %. Carbon nanotubes (CNTs) possess high electrical conductivity and ample lithium storage space. Sugiawati et al.[55] deposited p-sulfonated poly(allyl phenyl ether) (SPAPE) onto CNTs by electropolymerization. Compared to pure CNTs, SPAPE-coated CNTs increase the interfacial area between the electrolyte and the electrode, thus improving charge transfer efficiency. When used as the anode with a lithium metal counter electrode, SPAPE-coated CNTs exhibited a high reversible capacity of 508 mAh g^{-1} (187 μAh cm^{-2}) at a 10 C rate over 500 cycles.

Similar with constructing a protective layer for electrode materials in LIBs, a protective layer for lithium metal batteries can also be designed through in situ polymerization within the

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electrode. Here, Li dendrite growth has been a persistent issue affecting the commercial application of lithium metal anode. Chu et al.[58] conducted in situ electropolymerization on the surface of lithium metal anode to create a layer composed of an ordered array of L-tyrosine. The carboxyl group on L-tyrosine makes it easier for DME to form hydrogen bonds, thereby altering the solvent structure of the electrolyte. Furthermore, the reduction of free DME allows more $TFSI^-$ ions to participate in the formation of the solid electrolyte interface (SEI) film, increasing the proportion of LiF in the film. As a result, with 2 wt% L-tyrosine, Li|Cu cells demonstrated improved stability for up to 200 cycles with an average Coulombic efficiency (CE) of 93.1% in ether electrolytes, and Li||$Li_4Ti_5O_{12}$ (LTO) demonstrated excellent cycling capabilities with 119 mAh g^{-1} capacity retention after 500 cycles. Similarly, Zhang et al.[59] added an appropriate amount of acrylonitrile (AN) to the electrolyte and employed a similar method to form a polyacrylonitrile (PAN) artificial SEI on the surface of metallic lithium during cycling (Figure 4c). PAN facilitates uniform nucleation and growth of lithium deposition with significantly reduced side reactions. The structure and morphology of Li deposition is porous and composed of whiskers without AN and shows dense and uniform structure with AN (Figure 4d).

Electropolymerization has been also applied as cathode surface coating in LSBs. Guo et al.[16] carried out an electropolymerization of a conformal conjugated microporous polymer (CMP) nanoskin on the cathode framework. The CMP nanoskin is very thin and lightweight but can encapsulate both the electrolyte and active sulfur species in the electrode. As a result, the battery exhibits a high capacity (870 mAh g^{-1}) and long-term cycling (1000 cycles). Even under lean electrolyte conditions, the battery achieves an energy density of over 300 Wh kg^{-1}. Moreover, as the cathode hosts in lithium metal batteries often consist of porous materials, employing in situ polymerization within the electrode can yield superior results. Lee et al.[56] added aniline monomers to the electrolyte to make an in situ electropolymerization of polyaniline (PANI) through a single controlled charge protocol. PANI possesses a high electrical conductivity. Meanwhile, due to the plenty of positively charged amino-containing groups on its backbone, PANI also possesses a strong affinity for the soluble intermediates, polyselenides. The protective conductive layer reduces direct contact between the electrode and electrolyte, thereby suppressing the dissolution of polyselenides. Simultaneously, the functional groups in the porous structure capture lithium polyselenides through the strong interactions.

3.3. Other applications

Electropolymerization can be utilized to design intermediary layers and current collector modification layers with different functionalities. Compared to other methods, electropolymerization allows for easy control of the thickness of intermediary or modification layers. Similarly, the tunability of the molecular structure of organic compounds enables the design of a variety of functional layers.

Organic electrode materials are prone to dissolution in the electrolyte, leading to poor stability during cycling, which limits their practical application. Carbazole groups can undergo polymerization under the electric field and serve as high-voltage chemical reaction centers, effectively addressing the issue of organic electrode dissolution during cycling. Based on this concept, Zhao et al.[22] employed electropolymerization to prepare a new organic electrode, 4,4′,4′′-Tris(carbazol-9-yl)-triphenylamine (TCTA), as shown in Figure 5a. After immersing the TCTA organic electrode in an organic electrolyte (1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC): diethyl carbonate (DEC) mixture) for five days, FTIR and 1H NMR results revealed that no new substances were formed in the organic solution, indicating that TCTA does not dissolve into the organic solvent, thus exhibiting high stability. Little change of the morphology of pristine and cycled TCTA cathodes in voltage windows of 3.0–3.9 V further demonstrates the stability of TCTA (Figure 5b). Zeng et al.[23] prepared a porphyrin complex of [5,15-di(thiophen-2-yl) porphinato] M(II) (MTP, M = Cu, Ni) as the cathode for organic batteries. The S atom and the N atom within the porphyrin complex serve as active sites for storing both anions and cations. Due to the in situ polymerization of the thiophene groups during initial cycles, the stability of the cathode materials has been significantly improved. Moreover, the metal porphyrin complex possesses a multiple electron transfer capability. As a result, the CuTP cathode exhibits an excellent electrochemical performance with a reversible capacity of 203 mAh g^{-1} at 100 mA g^{-1} and long-term cycling stability of up to 11,000 cycles at 5 A g^{-1}.

In lithium batteries, liquid electrolytes have the drawback of low flash points and high gas release, making them prone to self-ignition and explosions during use. This has always been a significant safety concern for batteries. In contrast, solid-state electrolytes offer higher chemical and thermal stability, significantly improving battery safety. Poly(ethylene oxide) (PEO)-based polymer electrolytes are known for their excellent flexibility, mechanical strength, good interface contact, and compatibility with lithium metal anodes, making them a subject of extensive research.[98,99] However, the limited oxidative resistance of the ether functional groups on PEO restricts its compatibility to electrode materials with lower voltage platforms. The method of constructing a buffer layer between the electrode and the polymer electrolyte through electropolymerization to enhance the electrochemical oxidation window of the battery provides a new direction for the improved application of polymer solid-state electrolytes to high-voltage electrode materials. Li et al.[60] addressed this challenge by preparing a high-voltage and stable solid-state interface layer between the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NCM811) cathode and the PEO-based solid polymer electrolyte. This interface layer based on polyfluoroalkyl acrylate was synthesized through in situ solvent-free bulk electropolymerization. The electrochemical oxidation window of the composite electrolyte was significantly increased from 4.3 V to 5.1 V. The ionic conductivity also increased to 1.02×10^{-4} S cm^{-1} at room temperature and 4.72×10^{-4} S cm^{-1} at 60 °C.

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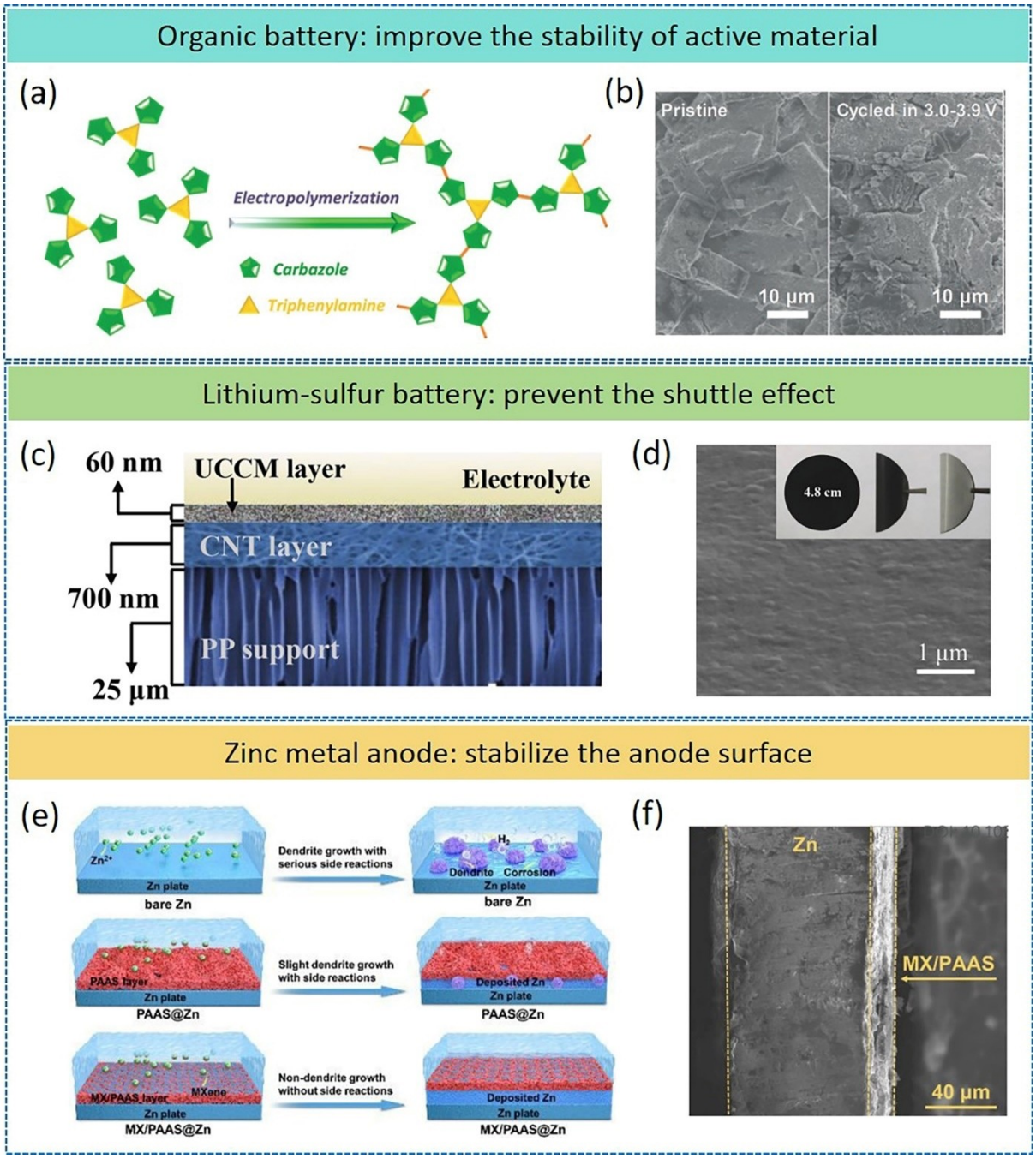

Figure 5. (a) Illustration of the electropolymerization process of 4,4′,4″-Tris(carbazol-9-yl)-triphenylamine (TCTA); (b) SEM images of pristine and cycled TCTA cathodes in voltage windows of 3.0–3.9 V; Reproduced with permission.[22] Copyright 2020, Wiley-VCH GmbH. (c) Illustration of the polycarbazole layer grown in situ on carbon nanotubes/polypropylene (CNT/PP) separator and application in LSBs; (d) The deposited ultrathin, compact, and conductive microporous (UCCM) polycarbazole membrane (inset: optical image of UCCM@CNT/PP separator); Reproduced with permission.[17] Copyright 2020, Elsevier. (e) Schematic illustration about Zn deposition on different electrodes; (f) Cross-sectional SEM images of the MXene/organic sodium polyacrylate (MX/PAAS)@Zn electrodes. Reproduced with permission.[18] Copyright 2023, The Royal Society of Chemistry.

Guo et al.[17] also utilized carbon nanotubes (CNT) as a substrate and conducted electropolymerization to create a polycarbazole-type ultrathin, compact, and conductive microporous (UCCM) interlayer to modify the polypropylene (PP) separator (Figure 5c). A compact membrane with thickness of around 60 nm was grown on the CNT/PP support (Figure 5d). The membrane exhibits high electronic conductivity, with an electron conductivity of up to 23 $S\,m^{-1}$. Additionally, the membrane contains nanochannels of around 0.82 nm in size, facilitating the rapid transport of ions while limiting the passage of polysulfide molecules. The characteristic peaks of Li_2S_n species appear on the surface of CNT/PP separator facing the Li metal PP separator. The nearly zero shuttling current confirms the electrochemical advantages of preventing shuttle effect.

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The interlayer often requires sufficient conductivity and good mechanical properties. Combining the electrodeposition of inorganic conductive materials with organic electropolymerization can conveniently address this issue, resulting in a uniform hybrid film. Wang et al. electro-polymerized an inorganic conductive layered MXene and organic sodium polyacrylate (PAAS) composite film on the surface of zinc metal (Figure 5e).[18] SEM images show that the MXene@PAAS composite film closely adheres to the zinc metal, with a thickness of approximately 10 μm (Figure 5f). The composite film can effectively adsorb zinc ions, enabling the uniform deposition of zinc ions on the negative electrode surface and eliminating the growth of dendrites.

4. Summary and Outlook

Electropolymerization, serving as a convenient and efficient strategy for electrochemical synthesis of conductive polymers, provides extensive promising potential for improving the practicality and sustainability of next generation energy storage devices from ion/charge transport/storage and interface engineering. Various polymer materials based on electropolymerization have attracted great attention in applications including but not limited to LIBs, ZIBs, LSBs, and supercapacitors, etc. In this mini review, we have summarized the recent applications of various polymers synthesized based on electropolymerization in energy storage devices. A comprehensive discussion was provided on the optimization of the processes and underlying mechanisms concerning their utilization in organic electrodes, intermediate layers, and protective layers. The following is a summary of these contents.

1. The introduction of electropolymerization not only addresses the intrinsic drawbacks of poor rate performance and low utilization of organic electrodes, but also effectively resolves the dissolution issue of organic materials in the electrolyte. Furthermore, the self-supporting organic electrode obtained by electropolymerization avoids the capacity dropping caused by the easy dissolution and breakage of traditional electrodes. Combined with its ultra-thin and cross-linked structure, it synergistically achieves high energy density and stability of organic batteries. In additional, due to its unique free-standing property as electrode material, it reduces the use of additional conductive additives and binders, lowering the mass of inactive materials in the electrode and thereby increasing energy density.

2. The interface between electrodes and electrolytes serves as the site for numerous intricate chemical reactions and is the focal point of various physical and chemical interactions. It directly influences the electrochemical performance and durability of batteries. A well-designed interfacial layer by electropolymerization can prevent the direct contact between the electrolyte and the electrode. Synchronized optimization of strength and toughness is achieved through distinctive structural forms and interface characteristics. In situ growth enhances the adhesion between the layer and the substrate. Electropolymerization facilitates a tighter integration between electrode materials and current collectors. This leads to improved electron transfer efficiency and enhanced utilization of the electrode material.

3. In the realm of separator modification, electropolymerization offers the following advantages: 1) Ordered and controllable morphologies that facilitate ion/electron conduction; 2) Most exhibit tunable hydrophilicity, enhancing the wetting properties of the modified membrane towards the electrolyte, thereby further improving electrochemical performance; 3) Capability to enhance the puncture resistance of the membrane, extending the cycle life of energy storage devices.

4. Electropolymerization can be employed for the fabrication of functional protective layers on electrode materials. In the case of high-voltage electrode materials, in situ polymerization can generate protective layers to shield against the corrosive effects of the electrolyte. In the anode, particularly for metallic lithium, in situ polymerization can establish protective layers that hinder the excessive consumption of the electrolyte and the uncontrolled growth of lithium dendrites.

5. Accurately revealing the mesostructure and microregion reactivity of electrode materials without compromising the electrode structure requires advanced operando spectroscopic and electrochemical characterization techniques. There are also specific requirements for the accessibility, structural integrity, and ease of operation of the electrode. Thanks to the development of electropolymerization, operando characterization techniques is easy to applied in electrodes.

Nonetheless, the development of electropolymerization for energy storage devices faces numerous challenges, including enhancing the synthesis pathways for electropolymerization, investigating the impact of the microenvironment on electropolymerization chemical kinetics, exploring lithium ion transport mechanisms in multiphase systems, employing advanced characterization techniques, and iterating on large-scale production processes. Herein, some perspectives and prospects for maximizing the promising potential of electropolymerization to realize new sustainable batteries and supercapacitors.

1. More research is needed to develop organic electrode materials that are well-suited for electropolymerization. The focus should be on expanding the range of available electrode materials, particularly those with high capacity and high working voltage, to meet the diverse requirements of different energy storage applications.

2. A deeper investigation into the factors influencing the affinity between polymers and substrates is essential. Gaining a more comprehensive understanding of this interaction will help identify universal substrates that can be effectively employed in electropolymerization processes.

3. Electropolymerization methods need to be further developed and adapted for use in a wider range of battery systems. This includes exploring their applications in sodium-ion batteries, potassium-ion batteries, magnesium-ion batteries, and solid-state electrolytes. This expansion of scope will facilitate the use of electropolymerization in a broader array of energy storage technologies.

4. The synthesis strategies of electropolymerization urgently need optimization concerning their sustainability, environmen-

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tal friendliness, as well as compatibility with energy storage components.

5. Polymers with controlled monomer sequence are more advantageous for regulating ions plating/stripping and material transport. The preparation and synthesis of such polymers constitute one of the most challenging tasks. Although electropolymerization has demonstrated promising potential in controlled synthesis, its application across different substrates and systems necessitates more comprehensive experimental and theoretical investigations.

6. As a simple strategy widely used to prepare flexible electrodes, membrane electrodes prepared by electropolymerization usually have excellent flexibility, mechanical strength, and tunable electrocatalytic sites. Some monomers suitable for preparing flexible batteries based on electropolymerization strategies include 3,4-ethylenedioxythiophene (EDOT), triphenylamine (TPA), diludine, tetrahydrofuran, benzodifurandione, etc. They have an inherent aromatic structure and abundant functional groups, which impart good electrical conductivity while endowed with a solid skeleton and excellent ion transport/storage kinetics.

In summary, while electropolymerization offers numerous advantages for the development of self-supporting electrodes and functional layers in energy storage devices, addressing these challenges and advancing the technology are crucial for its continued growth and impact in the field of energy storage. Researchers are encouraged to work on these aspects to unlock the full potential of electropolymerization in various battery systems and energy storage applications.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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