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Review

Electrochemically Active Polymer Components in Next-Generation $LiFePO_4$ Cathodes: Can Small Things Make a Big Difference?

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Abstract: As a cathode material for lithium-ion batteries, lithium iron phosphate ($LiFePO_4$, LFP) successfully transitioned from laboratory bench to commercial product but was outshone by high capacity/high voltage lithium metal oxide chemistries. Recent changes in the global economy combined with advances in the battery pack design brought industry attention back to LFP. However, well-recognized intrinsic drawbacks of $LiFePO_4$ such as relatively low specific capacity and poor electronic and ionic conductivity have not yet been fully mitigated. Integration of electrochemically active electron-conducting polymers (EAECPs) into the cathode structure to replace conventional auxiliary electrode components has been proposed as an effective strategy for further performance improvement of LFP batteries. In this review, we show how various combinations of polymer properties/functions have been utilized in composite $LiFePO_4$ electrodes containing EAECP components. We present recent advances in the cathode design, materials, and methods and highlight the impact of synthetic strategies for the cathode preparation on its electrochemical performance in lithium-ion cells. We discuss advantages and limitations of the proposed approaches as well as challenges of their adoption by the battery manufactures. We conclude with perspectives on future development in this area.

Keywords: lithium iron phosphate; lithium-ion batteries; cathode material; electrochemically active polymers; electron-conducting polymers

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1. Introduction

Lithium-ion batteries (LIBs) are now used extensively for an increasingly diverse range of applications, from portable electronics and power tools to hybrid and electric vehicles, utility-scale energy storage and aerospace industry [1–3]. The energy and power density, cycle life, safety and cost of LIBs are often decided by the properties of one of their key building blocks, the cathode active material. Under rapidly growing demands from the industrial and consumer sectors, considerable efforts have been devoted to developing novel positive electrode materials and improving the functional performance of existing cathode formulations [4–6].

After the first-generation cathode material, lithium cobalt oxide $LiCoO_2$, was commercialized by Sony in the early 1990s, a large variety of LIB cathode chemistries such as layered lithium transition metal oxides (LMO) (lithium nickel manganese cobalt oxides (NMC) or lithium nickel cobalt aluminum oxides (NCA)) [7,8] and manganese based spinel compounds [9] have emerged (see Table 1 for a full list of acronyms and abbreviations). In 1997, Goodenough and colleagues first reported the use of lithium iron phosphate ($LiFePO_4$, LFP) as a cathode material for lithium-ion batteries [10]. LFP has fast evolved into a commercial product, largely because of the unique and advantageous combination of properties, including competitive theoretical capacity (170 mAh/g), stable redox potential (3.5 V vs. Li^+/Li), excellent stability to electrochemical cycling, low cost, natural abundance, environmental benignity, thermal stability and safety even in the over-charging and over-discharging states [11–13]. Unmatched stability and safety immediately made lithium iron phosphate a favorable LIB cathode material over competitors. However, due to inherent drawbacks of LFP (poor electronic conductivity, slow lithium ion diffusion, low tap density), the research and development focus gradually shifted towards advanced LMO chemistries that offered superior electrochemical performance. While NCM/NCA developers are still working on mitigating serious safety risks associated with these materials [8], recent advances in cell-to-pack technology have significantly narrowed the energy density gap between LFP and LMO batteries [3,14]. In this situation, cost considerations have become a decisive factor, and nearly all major automotive LIB manufacturers have already announced switching to lithium iron phosphate battery chemistry. The low conductivity-related drawbacks of $LiFePO_4$ have not, however, been fully mitigated, which imposes some performance limitations, for example, on the battery charging rates.

Table 1. Acronyms and Abbreviations.

Abbreviation	Definition
ANI	Aniline
B	Binder
CA	Conductive additive
CB	Carbon black
CCTS	Carboxylmethyl chitosan
C-LFP	Lithium iron phosphate, carbon-coated
CMC	Carboxymethyl cellulose
C-PPy	Cross-linked polypyrrole
CRGO	Chemically reduced graphene oxide
D3PIE	Dynamic three phase interline electropolymerization
EAECP	Electrochemically active electron-conducting polymer
EAECP-C-LFP	Carbon-coated lithium iron phosphate particles additionally coated with electrochemically active electron-conducting polymer
EAECP-LFP	Pristine lithium iron phosphate particles coated with electrochemically active electron-conducting polymer
EAECP-$LiFePO_4$	Lithium iron phosphate particles coated with electrochemically active electron-conducting polymer
EDOT	3,4-ethylenedioxythiophene
FP	Polynorbornene polymer with fluoflavin pendant groups
LFP	Lithium iron phosphate, pristine (without carbon coating)
LIB	Lithium-ion battery
$LiCoO_2$	Lithium cobalt oxide
$LiFePO_4$	Lithium iron phosphate
Li-PANI	Polyaniline lithiated by treating with n-butyllithium
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
LMO	Layered lithium transition metal oxide
MWCNTs	Multi-wall carbon nanotubes
NCA	Lithium nickel cobalt aluminum oxide
$[Ni(CH_3\text{-salen})]$	N,N'-bis(3-methylsalicylideneiminate) nickel(II)
NMC	Lithium nickel manganese cobalt oxide
NMP	N-methyl pyrrolidone
P2b	Ethylene oxide-functionalized poly(TEMPO-substituted glycidyl ether)
PANI	Polyaniline
PANI:CSA	Camphorsulfonic acid-doped polyaniline
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEDOT:p-Tos	p-toluene sulfonate-doped poly(3,4-ethylenedioxythiophene)
PEDOT:p-TSA	p-toluene sulfonic acid-doped poly(3,4-ethylenedioxythiophene)
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)

Table 1. *Cont.*

Abbreviation	Definition
PHTPA	Hyperbranched poly(triphenylamine)
POMA	Poly-o-methoxyaniline
PPDI	Perylene diimide-functionalized polyacrylate
PProDOT	Poly(3,4-propylenedioxythiophene-2,5-dicarboxylic acid)
PPy	Polypyrrole
ProDOT	3,4-propylenedioxythiophene-2,5-dicarboxylic acid
PTFE	Polytetrafluorethylene
PTh	Polythiophene
PTMA	Poly(2,2,6,6-tetramethyl-1-piperinidyloxy-4-yl methacrylate)
PTPA	Poly(triphenylamine)
PVDF	Polyvinylidene fluoride
r-PANI	Reduced polyaniline
SA	Sodium algenate
SBR	Styrene-butadiene rubber
SDS	Sodium dodecyl sulfate
SPPO	Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide)
SWCNTs	Single wall carbon nanotubes
TEMPO	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl
Tr	Triton X-100

Several strategies for performance improvement of LFP cathodes have been suggested: (i) at chemistry level: ion doping [15]; (ii) at material level: particle morphology and size control [12,16], surface coating and modification [17]; (iii) at electrode level: development of auxiliary components [18,19] and electrode designs [20]. The industry adopted mass production methods for mitigating inherent drawbacks of lithium iron phosphate include carbon coating of $LiFePO_4$ particles, control of primary and secondary particle size, addition of relatively high amounts of carbon black (CB) to the cathode formulation and carbon coating of the current collector. Altogether, these methods help enhance the conductivity and increase the utilization of active material in LFP cathodes.

The $LiFePO_4$-based cathodes are usually made by dispersing active material, a conductive additive (CA) and a binder (B) in an appropriate solvent to form homogeneous slurry. The slurry is then spread onto the current collector; the coated electrodes are then dried and pressed (calendared) to obtain the target active layer thickness. The components of conventional LFP electrodes are shown in Figure 1.

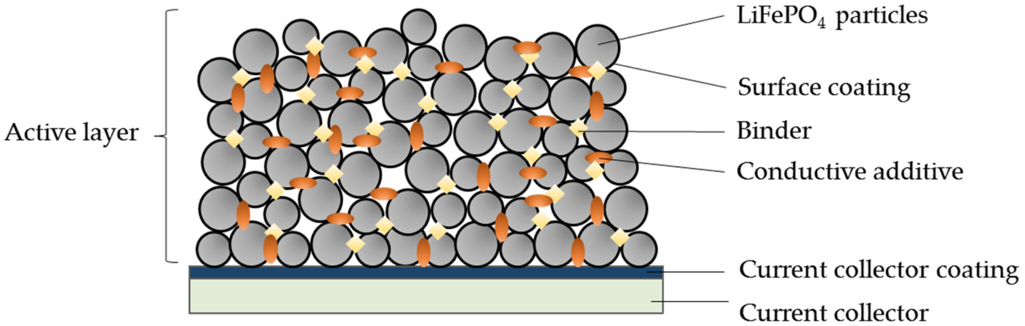

Figure 1. A conventional LFP electrode design.

The only component that stores charge in the battery cathode is $LiFePO_4$ active material. Its content in commercial electrodes is kept at 90 + wt%. All other components (active material coating, conductive additive, binder, current collector) are auxiliary as they do not contribute to charge storage and are added to the cathode only to enable the active material to perform its charge storage function. All auxiliary components play vital roles but at the same time they constitute "dead weight and volume", which inevitably leads to a loss in the specific capacity of the cathode.

In this review, we summarize various aspects of an elegant approach to "reviving" the "dead weight and volume" of LFP cathodes by replacing conventional auxiliary electrode components with electrochemically active electron-conducting polymers (EAECPs). The question that we will attempt to answer is whether substantially improved battery performance can be expected from making material changes to no more than 10 wt% of the electrode. Before highlighting main directions of research efforts in the integration of EAECP components into the $LiFePO_4$ cathode structure, we will first take a closer look at the main functional properties of these polymers that enable them to be considered as viable replacement for the structural elements of conventional electrodes.

2. Electrochemically Active Electron-Conducting Polymers (EAECPs): Function-Enabling Properties

Electrochemically active polymers are polymers that are prone to reversible oxidation or reduction by modulating their electrochemical potential. The ability to exchange electrical charges between fragments in different redox states makes these materials electroconductive. In this review, we are focusing on the polymers that are electrochemically active at potentials of $LiFePO_4$ cathodes operation that usually lie in the 3–4.3 V vs. Li/Li^+ region. Under these conditions, the vast majority of materials studied in this field are in a neutral, i.e., "reduced" or "undoped" state at low potentials and in an oxidized, i.e., "doped" state at high potentials. Below, we briefly discuss electrochemically induced changes in the EAECP properties upon switching from the neutral to the oxidized state. For a more detailed insight into the topic, the readers are referred to several excellent reviews [21–23].

Electrochemical oxidation of a neutral polymer leads to the formation of positively charged fragments in the polymer structure, often called "polarons" in conjugated systems. In the general case, this charge is electrostatically compensated by an anion that enters into the polymer bulk from the surrounding electrolyte. However, when "self-doped" polymers with grafted anionic functional groups in the backbone or blends of electrochemically active polymers with immobile polyanions, for example poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), are subjected to electrochemical oxidation, the charge compensation occurs via expulsion of mobile cations that compensate the negative charges of immobile anions in the neutral polymer. When ionic movement is restricted, the electrochemical activity is suppressed [24], which may be the reason of rarely observed electrochemical activity of the commercially available and hence widely used PEDOT:PSS material.

For classical conjugated systems like polyacetylene and polyheterocycles, the charge is delocalized over several monomer fragments, while for classical redox polymers, like polyvinylferrocene or stable radical TEMPO-based structures, the charge is strongly localized on one monomer fragment. This difference in the extent of charge localization/delocalization defines a drastic difference in many properties between these two classes of electrochemically active polymers, conjugated and redox ones. At the same time, many similarities between these two formally distinct classes of EAECPs can be found. While both types of electrochemically active polymers exhibit negligible conductivities in the neutral state, conjugated polymers may possess extremely high conductivities at the level of 1×10^3 S/cm whereas redox polymers are modestly conductive up to a few 1×10^{-2} S/cm [25,26]. This difference is dictated by two different modes of conductivity: free movement of charge in the conjugated systems and hopping between neighboring redox centers. At the same time, in many real conjugated polymer-based systems conductivity is limited not by the fast in-chain conductivity, but by the low interchain conductivity that is hopping-like. As an opposite example from the redox polymer world, it has been shown that redox radical polymers can exhibit high conductivities by very fast hopping at short (less than 600 nm) distances in dense aggregates [27].

The maximum reversible doping level for conjugated systems is ordinary about 1/3, while 1 is quite common for redox polymers. A sigmoidal shape is a common conductivity vs. potential (doping level) dependence for conjugated polymers, i.e., the neutral polymer becomes highly conductive at low doping levels (a few percent) and remains in a highly conductive state at further doping. For redox polymers, a bell-like shape of conductivity vs. potential is usually observed. The maximum conductivity is located at $\frac{1}{2}$ doping level, as the highest rate of charge transfer between localized redox centers is observed at equal concentration of neutral and oxidized sites. Further doping up to the level of 1 decreases the conductivity of redox polymers back to insulation levels in most cases. At the same time, extending the potential window of conjugated polymer stability by proper substitution or solvent choice may yield both deeper doping up to level 1 and a decrease in conductivity at high doping levels. In certain cases, redox polymers with multiple available redox states display multiple overlapping bell-shaped conductivity vs. potential (doping level) profiles that mimic the conductivity profiles of conjugated polymers charged to extremely high doping levels.

Though often considered as opposites, both conjugated and redox polymers have similar properties that enable their use as cathode active materials: high reversible redox capacity, i.e., electrochemical activity, electronic and ionic conductivity. Gravimetric capacities found for best polymers are in the same range as for traditional cathode materials for Li-ion batteries: as high as 223 mAh/g is reported for a phenazine-based polymer [28] and 230 mAh/g is reported for lithium emeraldine [29]. It is worth to note that while these materials are often proposed as the main active materials in Li-ion cells, they can properly function only in excessive electrolyte conditions because of the anion type of doping [30]. However, considering these materials as auxiliary LIB cathode components with the loading of a few wt% is viable even in industry-relevant cells that contain limited amount of electrolyte.

Both redox and conjugated polymers can be prepared via chemical and/or electrochemical polymerization techniques. The electrochemical polymerization is often preferable at the lab scale due to ease of film growth control via current/potential and the ability to grow polymer directly on a current collector for further electrochemical studies without any processing. A chemical route is the best choice if large amounts of polymer are needed, but the development of processing technology is often required in this case, which is usually beyond the scope of academic research.

Generally, EAECPs exhibit good adhesion to a variety of substrates and are considered as a “soft matter” [31], but higher than aluminum strength is found for typical electrochemically active electron-conducting polymers when prepared in special synthetic conditions [32]. Electrochemical doping of these materials may lead to swelling, which affects their mechanical properties [33,34].

The possibility of fine tuning all of the above described functional properties of EAECPs via selecting monomer chemistries and synthetic conditions provides the researchers with an attractive opportunity to prepare application-specific polymer networks with optimized performance in target environments. In particular, EAECPs exhibiting enhanced electronic/ionic conductivity, redox capacity, electrochemical, mechanical, and thermal stability in LIB electrolytes at potentials overlapping the operative redox couple of $LiFePO_4$ and good adhesion to the LIB cathode materials have been developed. This combination of properties potentially enables them to perform conductive, binding, and energy storage functions and replace conventional conductive additives, binders and coatings in various cathode designs. EAECP incorporation into LFP-based cathodes of Li-ion batteries should not potentially influence the recycling of spent batteries. The vast majority of these polymers are organic and as all other organic components of batteries, they are either fully destroyed during the pyrometallurgical recycling process or do not hamper metal ion separation in the hydrometallurgical recycling process. As a result, EAECPs have been proposed by the research community for use as various auxiliary components in the composite $LiFePO_4$ cathodes.

3. EAECP-Based Cathode Components

The following types of EAECP-based components of $LiFePO_4$ cathodes have been described in the research literature: (i) conductive coatings on $LiFePO_4$ particles; (ii) conductive binders; (iii) conductive current collector coatings. Most commercially available lithium iron phosphate materials employed for cathode preparation by different authors are carbon-coated and will be referred to as C-LFP in the following discussion whereas non-coated samples will be referred to as LFP. When the presence of carbon coating on LFP particles was not specified by the authors or when generally addressing lithium iron phosphate as an active material, the chemical formula of the compound ($LiFePO_4$) will be used.

3.1. EAECPs as Lithium Iron Phosphate Coatings

Coating $LiFePO_4$ particles with carbon is a commonly employed industrial method for improving electronic conductivity, electrochemical properties, and cycling stability of the active material [35]. However, carbon is electrochemically inactive so it adds to the "dead weight and volume" in the battery cathode, which inevitably leads to a loss in its specific capacity. Additionally, uniform and homogeneous carbon coatings on irregularly shaped primary and secondary $LiFePO_4$ particles are difficult to achieve, which limits the power performance enhancement capabilities of this approach. The carbon coating procedures are usually conducted at high temperatures, which could negatively affect the intrinsic properties of lithium iron phosphate and trigger the formation of secondary phases in the active materials [36].

Researchers have shown that EAECP coatings on $LiFePO_4$ particles potentially could perform the same functions as carbon coatings, be applied under milder conditions, and provide additional advantage of enhanced ionic conductivity of the active material. This section covers EAECP-coated $LiFePO_4$ materials that are isolated in the form of solid powders before being combined with conductive additives and/or binders to prepare cathodes, usually via a conventional slurry coating technique. Since carbon-coated lithium iron phosphate is usually referred to as C-$LiFePO_4$, we address polymer-coated compositions as EAECP-$LiFePO_4$. More specifically, bare LFP coated with a polymer is referred to as EAECP-LFP, and polymer-coated C-LFP is referred to as EAECP-C-LFP. The values of specific capacities for various cathode formulations are calculated based on the mass of active material (EAECP-$LiFePO_4$ or $LiFePO_4$).

The EAECP coatings on $LiFePO_4$ powders can be classified into two groups based on the synthetic method applied in their preparation. The research in this field is discussed in detail below; representative cases are highlighted in Table 2.

3.1.1. EAECP-Based Coatings by In Situ Chemical Polymerization over $LiFePO_4$ Particles

This group includes EAECP coatings produced by in situ oxidative chemical polymerization of the monomers in the presence of $LiFePO_4$ particles so that the polymer if formed on the particle surface. The polymerization process can be conducted by a solvent-free method [37] or a wet chemical technique [38–61]. Most of the disclosed techniques utilize an external oxidant [37,40–61] but in some cases, the intrinsic oxidation properties of delithiated lithium iron phosphate are used to drive the polymerization [38,39].

In a conventional wet chemical polymerization approach, $LiFePO_4$ powder, the monomer and optionally the doping agent are dispersed in the solvent. The oxidant is added to the solution, and the mixture is left reacting. After the completion of the polymerization, the formed precipitate is washed and dried to obtain EAECP-$LiFePO_4$. Both bare LFP powders and carbon-coated C-LFP materials were used as starting materials for the preparation of EAECP-coated samples. Coating $LiFePO_4$ particles with polypyrrole (PPy) [40–49], polyaniline (PANI) [40,50–57], polythiophene (PTh) [58], and poly(3,4-ethylenedioxythiophene) (PEDOT) [59,60] has been described using the in situ chemical polymerization method.

To polymerize pyrrole on the surface of LFP [41–43,45,46,48,49] or C-LFP particles [40,42,44,47], different oxidants ($FeCl_3$ [41–45,48,61], Fe(III) p-toluenesulfonate [46,47], $(NH_4)_2S_2O_8$ [40]) have been used in the reaction mixture. The thickness of the obtained PPy coating on the $LiFePO_4$ surface varied from 5 nm [46] to 100 nm [61], and the PPy content in the resulting composite powders varied from 1 wt% [46] to 21 wt% [43,45,61]. The influence of the conducting polymer content on the electrochemical performance of PPy-$LiFePO_4$ was investigated in several studies [40,41,46]. Wang et al. [41] and Huang et al. [40] used in-house synthesized LFP powder and commercial C-LFP powder, respectively, as a coating substrate. In these studies, composite samples with the weight contents of PPy equal to 5, 10, and 20 wt% [41] or 3, 7, and 13 wt% [40] were prepared. It was shown that at the PPy content of 10 wt% [41] and 7 wt% [40], the composites demonstrated the most improved discharge capacity, rate capability, and cycling stability over the parent $LiFePO_4$ formulation. Gao et al. [46] applied an ultra-thin (5 nm) polypyrrole coating onto in-house synthesized LFP nanorods and obtained composite powders containing 1.16 wt%, 2.95 wt%, 3.60 wt%, and 4.39 wt% PPy. The PPy-LFP containing 2.95 wt% polymer was determined as the optimal formulation, delivering enhanced electrochemical performance as compared to the non-coated sample. In all studied PPy-$LiFePO_4$–based electrodes, the polymer created a three-dimensional electronically and ionically conducting network between $LiFePO_4$ particles, which led to enhanced conductivity and better active material utilization. As a result, at the optimal PPy:$LiFePO_4$ weight ratio, the composites showed higher specific capacity, improved rate and cycling performance versus non-coated samples. When the amount of the polymer was smaller than optimal, it could not completely coat the $LiFePO_4$ particles, and the improvement in the conductivity of the material was limited. The excessive PPy coating (~70 mAh/g) reduced the specific capacity of the composites and inhibited ionic transport in the material [40,41,46]. The highest low-rate specific discharge capacity of the prepared PPy-$LiFePO_4$ materials varied in different studies from 132 mAh/g [41] to 153 mAh/g [42,46] and seemed to be largely defined not only by the coating properties but also by the type of the starting $LiFePO_4$ material, cathode composition, morphology, structure, and experimental conditions. Highly conductive PPy-$LiFePO_4$ was also shown exhibit improved cycling performance at low [46] and high temperatures [47]. The latter was attributed to higher tolerance of PPy-containing electrodes to mechanical stresses and minimized iron dissolution from the polymer-coated active material. Besides being able to perform in standard liquid electrolyte-based cells, PPy-$LiFePO_4$ was also found to support operation of a flexible thin battery with gel polymer electrolyte [48].

The polymerization of aniline on the $LiFePO_4$ surface has been accomplished using different oxidants such as $FeCl_3$ [50] [Lei 2009], $KMnO_4$ and $K_2Cr_2O_7$ [53], in the presence of different acids (H_3PO_4 and H_2SO_4 [51]) but the ammonium peroxydisulfate $(NH_4)_2S_2O_8$ in combination with HCl showed best results [53] and was used for the preparation of PANI-$LiFePO_4$ composites from LFP [56] or C-LFP [40,51–55]. Chen et al. suggested that PANI and C-LFP particles formed a composite through a self-assembly process [52]. The alkalescent aniline formed $[Ph\text{-}NH_3]^+Cl^-$ salt in the presence of HCl in the aqueous solution of reagents. With no $LiFePO_4$ particles in the reaction mixture, micelles composed of these salts served as a soft template for the PANI formation. In the presence of C-LFP particles, the micelles adsorbed on their surface acted as a hard template for the polymerization process yielding PANI-C-LFP composites (Figure 2). None of the above cited studies described any polymer-induced detrimental changes in the active material structure; on the contrary, during the polymer coating procedure, larger C-LFP particles were reported to split into smaller ones homogeneously coated by PANI, which could be advantageous for the electrolyte penetration into the active particles [52]. At the same time, it was also found that PANI-C-LFP powders could contain some uncoated areas and dissociative polymers, which could limit the performance of the composite material [54]. As in the case of PPy, using PANI for coating LFP and C-LFP materials helped improve their electrical conductivity, promote Li^+-ion diffusion and increase electrode tolerance to the mechanical stress during cycling. It was also suggested that PANI could mediate the polarity difference between other electrode components and the electrolyte thus making the active material particles more accessible to lithium ions [52,55]. Through this combined mechanism for performance improvement, reduced charge transfer impedance, higher specific capacity, rate capability, and cyclability were attained in the investigated PANI-$LiFePO_4$–based electrodes compared to the parent $LiFePO_4$ formulations [40,50–57]. Several studies showed that there was an optimal PANI content in the composite powder ranging from about 7 wt% [40,51] to 25 wt% [50], which yielded the best electrochemical performance. The low-rate specific discharge capacity for best performing samples was in the range from 140 mAh/g [50] to 165 mAh/g [51]. The PANI-C-LFP (7.3 wt% PANI)/CB/PTFE (75:20:5 wt%) electrode composed by Chen et al. [51] was able to discharge 123 mAh/g at 10C and showed less than 3% capacity fade over 100 cycles at C/5.

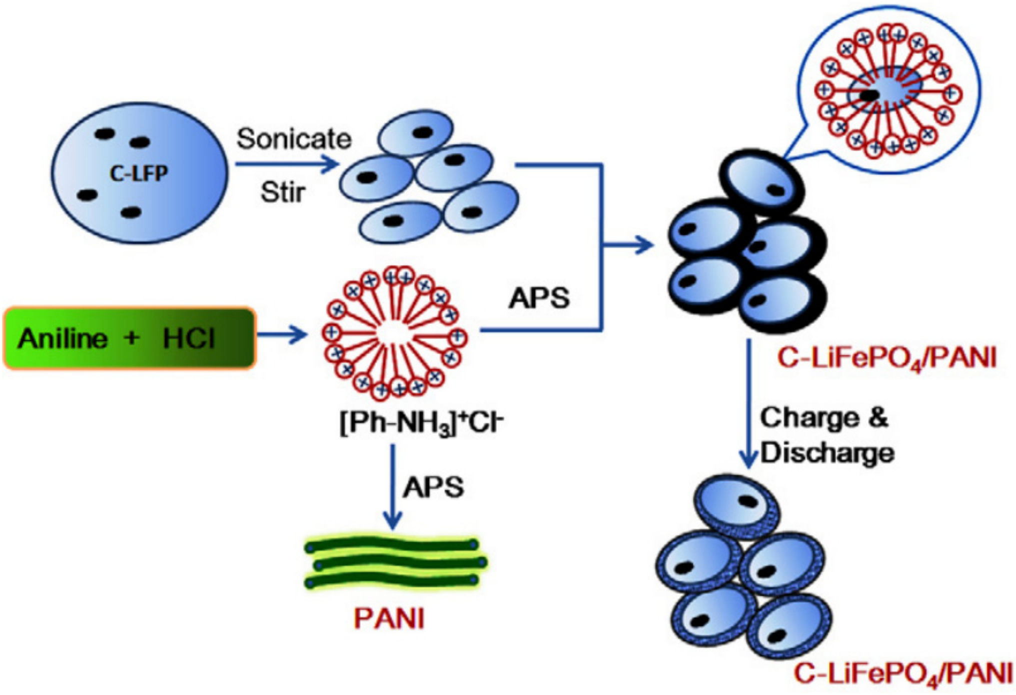

Figure 2. The formation mechanism for PANI nanofiber and PANI-coated C-LFP composite via a self-assembly process [52]. Reprint with permission from [52]; Copyright 2011, Elsevier.

Bai et al. prepared PTh-LFP powders by in situ polymerizing thiophene monomers on the surface of bare LFP particles ($FeCl_3$ was used as an oxidant) [58]. The composite material containing 10.56 wt% polythiophene yielded the highest electrochemical performance of the PTh-LFP/CB/PTFE (75:20:5 wt%) cathode, which demonstrated substantially improved specific capacity over the bare LFP-based counterpart in the C/12–1C range. In particular, the specific capacities at C/12 were found to be about 157 mAh/g for PTh-LFP and 127 mAh/g for bare LFP. The PEDOT-coated LFP powder was synthesized by Shi et al. in the form of $LiFePO_4$ particles conglomerated together by PEDOT into secondary particles with an average size of 2–3 µm [59]. The preservation of the conjugated polymer chains connecting LFP in these secondary particles was considered essential to achieving improved electrochemical performance and cycling stability of the electrodes. In a different study, C-LFP particles were pre-coated with nonionic surfactant Triton X-100 (Tr) prior to PEDOT deposition in an attempt to improve PEDOT adhesion and form a more uniform conductive coating [60]. As a result, an increase in specific discharge capacity relative to the starting C-LFP material was observed for the PEDOT-Tr-C-LFP sample containing 2.9 wt% PEDOT over the entire range of charge–discharge rates studied: the composite electrode discharged about 165 mAh/g at a current density of 20 mA/g and 81 mAh/g at 1600 mA/g.

The surface of $LiFePO_4$ materials has also been modified with composite EAECP-based coatings [42–45,49,54,57,61]. In several studies, polyethylene glycol (PEG) was introduced in the coating structure in an attempt to simultaneously improve the electronic conductivity and lithium ion diffusion rate of $LiFePO_4$ materials [42–45,54,61]. When applying PPy-based coatings to $LiFePO_4$, Fedorkova et al. added a small amount of PEG (PPy:PEG 33:1 wt%) to the reaction mixture in the beginning of polymerization to obtain PPy-PEG-coated $LiFePO_4$ samples with the polymer content ranging from 10 wt% [42,44] to 21 wt% [43,45,61]. The authors found that PPy-PEG coatings on $LiFePO_4$ particles improved both the transport of electrons along the resulting polymer network and the surface exchange of lithium ions due to the higher porosity and the salt-dissolving property of PEG. The presence of PEG also provided enhanced mechanical stability of PPy to volume changes during charge–discharge cycling. As a result, the introduction of PEG into the polymer coating of $LiFePO_4$ particles resulted in a higher specific capacity as well as in a better performance under high charge–discharge rates in comparison to conventional C-$LiFePO_4$ or PPy-$LiFePO_4$. The highest discharge capacity was demonstrated for the PPy-PEG(10 wt%)-C-LFP as a component of PPy-PEG-C-LFP/CB/PVDF (80:10:10 wt%) cathode: 156 mAh/g at C/5 and 97 mAh/g at 5C [42]. Gong et al. coated C-LFP particles with PANI:PEG copolymer via chemical polymerization of aniline in the presence of ANI-functionalized poly(ethylene glycol) mono-methyl ethers (mPEG) to obtain composite material containing 8.9 wt% PANI:PEG [54]. Compared with PANI-C-LFP, the 4 nm-thick PEG-containing coating layer appeared more uniform and complete, which was related to the additional roles of mPEG segments as stabilizers preventing C-LFP particles agglomeration and as hard templates in the co-polymerisation process. The homogeneous electron-and ion-conducting PANI:PEG coating delivered enhanced electrochemical performance of the composite material in a PANI:PEG-C-LFP/CB/PTFE (75:20:5 wt%) cathode. It delivered the initial specific capacity of 163.0 mAh/g and stable cycling at C/10 (95.7% capacity retention over 100 cycles) and retained 76.8% of its initial capacity (125.3 mAh/g) at 5C.

In other studies, $LiFePO_4$ powders were modified with binary coatings containing PANI [57] or PPy [49] in combination with chemically reduced graphene oxide (CRGO). In these cases, graphene oxide was used as the oxidizing reagent the in situ chemical polymerization of the monomers so that the as-produced CRGO and the conducting polymer deposited simultaneously on the $LiFePO_4$ surface. The resulting composites showed high specific capacity at C/5 (>160 mAh/g) and still delivered almost 80 mAh/g at 20C, which was a significant improvement over baseline samples. Excellent rate capability of PPy-CRGO-LFP cathode was attributed to high Li^+ diffusion coefficient and pronounced electronic conductivity originated from the synergetic effects of PPy and CRGO in the LFP coating [49].

Contrary to the above described techniques that require the use of an external chemical oxidant to deposit EAECP over $LiFePO_4$ particles, another approach implying spontaneous polymerization of the starting monomers on the surface of delithiated $LiFePO_4$ has also been developed [38,39]. Lepage et al. suggested delithiating $LiFePO_4$ with the help of hydrogen peroxide to produce solid $Li_{(1\text{-}0.3)}FePO_4$, which was then dispersed together with EDOT monomer in the methanol solution of LiTFSI and left reacting to yield PEDOT-LFP composite powder (Figure 3) [38]. The electrochemical tests performed on "no-carbon-added" PEDOT-LFP/PVDF (8:84.5:7.5 wt%) electrodes showed specific capacities of 163 mAh/g at C/10 and 123 mAh/g at 10C. The polyphenylene-coated LFP powder was prepared by Guo et al. in a one-step reaction of bare LFP and benzenediazonium tetrafluoroborate ($C_6H_5N_2{}^+BF_4{}^-$) in acetonitrile, which implied simultaneous delithiation of $LiFePO_4$ and the formation of reactive phenyl radicals undergoing spontaneous polymerization on the LFP surface [39]. Such produced polyphenylene coating enabled good electrochemical performance of micron-sized LFP particles, which is usually a challenge even when significant amounts of conductive additives are used in the cathode. The prepared composite material was tested in carbon-free polyphenylene-LFP/PVDF (90:10 wt%) electrodes and was able to deliver the discharge capacity of 165 mAh/g at C/10 and an improved high rate capability, even over the LFP/C/PVDF (80:10:10 wt%) baseline cathode. Results disclosed in [38,39] show the ability of the obtained coatings to fully replace the conventional conductive additive by accepting its functions in the electrode.

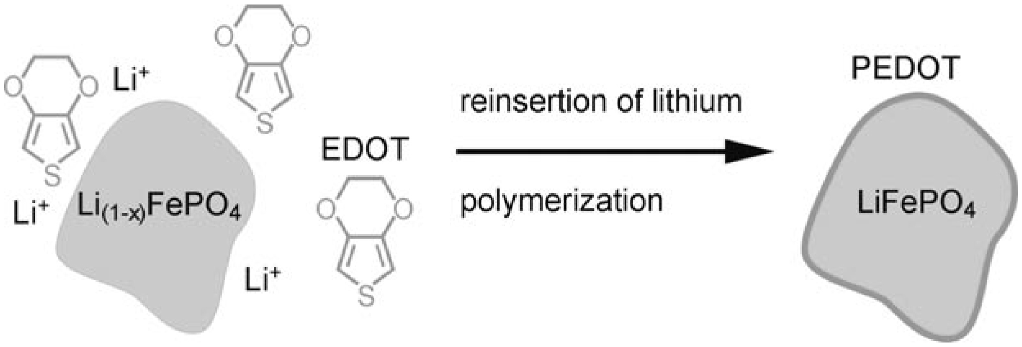

Figure 3. The polymerization reaction. The reinsertion of lithium into $Li_{(1-x)}FePO_4$ leads to the oxidation of EDOT, which is deposited on the solid surface as the conducting polymer PEDOT [38]. Reprint with permission from [38]; Copyright 2011, John Wiley & Sons, Inc.

Besides methods of wet chemical synthesis, a chemical vapor deposition (CVD) technique was also employed for the preparation of EAECP-coated $LiFePO_4$ powders. In particular, Gong et al. exposed a slurry containing C-LFP and Fe(III) tosylate as oxidant to the pyrrole monomer vapor to obtain PPy-C-LFP material with about 11.1 wt% PPy in the composite [37]. PPy-C-LFP/CB/PVDF and C-LFP/CB/PVDF electrodes with the same weight ratio of the components (75:15:10 wt%) were prepared and their rate capability was tested at −20 °C, 20 °C, and 55 °C. At −20 °C and 20 °C, the PPy-coated sample delivered higher discharge capacities than the pristine sample at 5C and higher rates. At 55 °C, the PPy coating enabled a much higher discharge voltage plateau and significantly improved the cycling performance of the electrode.

To summarize, in situ chemical polymerization is a simple method that allows to uniformly coat $LiFePO_4$ particles with ultrathin layers of EAECPs under rather mild conditions. The in situ approach provides uniform distribution of lithium iron phosphate material and prevents particles agglomeration. The thickness and morphology of the polymer coatings can be conveniently controlled by varying the synthetic conditions. At the same time, extensive measures may be required to prevent the oxidation of the active material and remove any contamination of the final product by external oxidants and reaction sub-products.

3.1.2. EAECP-Based Coatings by Mixing LFP with Ex Situ Synthesized Polymers

This group includes EAECP coating obtained on the $LiFePO_4$ particles by mixing the $LiFePO_4$ powder and the pre-synthesized polymer in solution [62–68] or in the dry phase [60,69,70].

Murugan et al. first demonstrated that as-prepared $LiFePO_4$ nanocrystals could be coated with p-toluene sulfonic acid (p-TSA) doped poly(3,4-ethylenedioxythiophene) (PEDOT) by simply mixing them with a colloidal solution of the polymer at ambient temperature [62]. The resulting PEDOT:p-TSA-LFP nanohybrids contained 8 wt% polymer, which evenly coated the LFP nanorods. The cathodes prepared from this material (PEDOT:p-TSA-LFP/CB/PTFE 75:20:5 wt%) exhibited high discharge capacity of 166 mAh/g at C/15, which was a 23% improvement over the pristine LFP-base cathode. PEDOT:p-TSA coating on LFP particles also enabled superior rate capability and cyclability of the electrode, which was explained by the improved kinetics and synergistic effects provided by the electronically and ionically conducting p-TSA-doped PEDOT. Dinh et al. used a blending method to coat PEDOT:p-TSA as well as PPy onto LFP particles of different size and morphology [63–65]. In the comparative studies [63,64], all polymer-coated samples showed much improved performance over the pristine materials; however, PEDOT:p-TSA coatings enabled slightly higher specific capacity of the polymer-coated LFP than PPy. The specific capacities of 167 mAh/g [64], 169 mAh/g [63], and 170 mAh/g [65] at 1C were observed for different in-house synthesized PEDOT:p-TSA-coated LFP architectures. Raj et al. used PEDOT doped with PSS anions to coat both pristine and carbon-coated $LiFePO_4$ powders in a one-step mixing procedure [66]. The LFP sample coated with 10 wt% PEDOT:PSS and the C-LFP sample coated with 5 wt% PEDOT:PSS showed the highest increase in conductivity (by 10^4–10^8 folds), about 10 fold increase in the Li^+ ion diffusion coefficient, and most enhanced electrochemical performance over the starting materials (LFP and C-LFP, respectively) when tested in the cathodes containing 10 wt% acetylene black and 10 wt% PVDF. The performance improvement was attributed to the PEDOT:PSS polymer providing conducting path for electron mobility and Li^+ ions diffusion. Su et al. coated the camphorsulfonic acid (CSA)-doped PANI onto the surface of C-LFP particles in m-cresol solution and also observed that charge–discharge capability of the cathodes was positively affected by PANI:CSA coating on the active material [67].

A solution blending technique was also used by Su et al. to coat C-LFP particle with a stable radical redox polymer polytriphenylamine (PTPA) [68]. The best electrochemical performance was found for the composite samples containing 10 wt% PTPA. When tested in the PTPA-C-LFP/CB/PTFE (70:20:10 wt%) cathode, the specific capacity of the polymer-coated material reached up to 154.5 mAh/g at C/10 and 114.2 mAh/g at 10C, which was higher than the capacities shown by the C-LFP samples at the same rates (146.4 mAh/g and 85.5 mAh/g, respectively). The enhancement of the capacity and rate capability of the composite material was attributed to the positive effect of the PTPA, which formed a supplementary electrochemically active coating on the surface of C-LFP particles and between particles, resulting in an improved electronic/ionic conductivity and the full utilization of active materials.

Ozerova et al. applied PEDOT coatings onto C-LFP particles and investigated the influence different surfactants onto the polymer deposition process [60]. The authors found that adding surfactants to the reaction mixture during polymer synthesis did not have any positive effect on the performance of the final composite powders. At the same time, preprocessing of C-LFP material with Triton X-100, a nonionic surfactant, lead to a considerable increase in the capacity of the synthesized composite relative to the starting C-LFP material over the entire range of cycling rates studied, including high current densities.

In an attempt to implement a solvent-free coating process, Ozerova et al. prepared PEDOT-LFP powder by grinding LFP and pre-synthesized and dried PEDOT but the resulting composite sample showed limited rate capability, which was attributed to the presence of considerably large PEDOT agglomerates hindering the ionic transport in the cathode [60]. In another study, the mechanochemical treatment of a dry mixture of C-LFP and the emeraldine base form of PANI enabled the formation of a hybrid nanocomposite with close to core–shell structure and improved electrochemical performance not only over the pristine LFP sample but also over the PEDOT-LFP prepared by mechanochemical polymerization of the aniline monomers on the LFP surface [69]. In the latter case, the composite material was believed to be adversely affected by the partial oxidation of Fe^{2+} ions of LFP by the ammonium persulfate oxidant during polymerization and/or by ammonium hydroxide treatment of the composite material performed for de-doping PANI. Another solvent-free coating method was developed by Ajpi et al. [70]. According to this method, C-LFP was mixed with pre-synthesized PANI and lithium acetate in a mortar and then thermally treated at 300 °C, for 1 h, in an Ar/H_2 (90:10) atmosphere yielding a crosslinked PANI coating on the C-LFP surface. PANI-C-LFP showed good rate capability with discharge capacities of 145 mAh/g at C/10 and 100 mAh/g at 2C, which meant 21% capacity enhancement at C/10 and 45% enhancement at 2C over the C-LFP sample without a polymer coating. As in the above discussed studies, the enhanced rate capability was attributed to the improved electronic and ionic conductivity promoted by the EAECP at the surface of the $LiFePO_4$ particles.

The discussed mixing techniques imply the use of pre-synthesized (in many cases, commercially available) EAECP formulations. The coating thickness is easy to control by varying the polymer concentration in the starting solution/dispersion. This represents a competitive advantage over in situ chemical polymerization. At the same time, a search for the proper less-impacting solvent for the process can be challenging.

Table 2. Synthetic strategies and electrochemical performance of polymer-coated lithium iron phosphate (EAECP-$LiFePO_4$) materials.

EAECP-$LiFePO_4$ Material	**Synthesis Route for EAECP-$LiFePO_4$ Material**	**Cathode Active Layer Composition**	**Initial Discharge Capacity, mAh/g (Per EAECP-$LiFePO_4$ Weight)**		**Capacity Retention, %/Number of Cycles (Discharge Current)**	**Reference**
			At Low Discharge Current (Discharge Current)	**At High Discharge Current (Discharge Current)**		
PPy (7 wt%)-C-LFP	In situ chemical polymerization over $LiFePO_4$ using an external oxidant in solution	PPy-C-LFP/CB/PTFE (75:20:5 wt%)	150 (C/10)	110 (10C)	99.3%/20 cycles (C/10)	[40]
PPy (2.95 wt%)-LFP		PPy-LFP/CB/PVDF (85:7:8 wt%)	153 (C/10)	118 (5C)	98.8%/20 cycles (C/10)	[46]
PANI (7 wt%)-C-LFP		PPy-C-LFP/CB/PTFE (75:20:5 wt%)	165 (C/5)	123 (10C)	97.4%/100 cycles (C/5)	[51]
PPy-PEG (appr. 10 wt%; 33:1)-C-LFP		PPy-PEG-C-LFP/CB/PVDF (80:10:10 wt%)	156 (C/5)	97 (5C)	100%/25 cycles (C/5)	[42]
PANI-CRGO-LFP (0.15:0.005:1, by weight)		PANI-CRGO-LFP/CB/PTFE (80:10:10 wt%)	165 (C/5)	70 (25C)	76.1%/1000 cycles (2C)	[57]
PEDOT (7.1 wt%)-LFP	In situ chemical polymerization over delithiated $LiFePO_4$ in solution	PEDOT-LFP/PVDF (8:84.5:7.5 wt%)	163 (C/10)	123 (10C)	close to 100%/30 cycles (C/2)	[38]
PPy (11.1 wt%)-C-LFP	CVD	PPy-C-LFP/CB/PVDF (75:15:10 wt%)	148 (1C) at 20 °C	80 (20C) at 20 °C; 135 (5C) at 55 °C	82%/700 cycles (5C) at 55 °C	[37]
PEDOT:p-TSA (8 wt%)-LFP	Mixing of $LiFePO_4$ and a polymer in solution	PEDOT:p-TSA-LFP/CB/PTFE (75:20:5 wt%)	166 (C/15)	120 (5C)	97%/50 cycles (C/15)	[62]
PEDOT:PSS (10 wt%)-LFP		PEDOT:PSS-LFP/CB/PVDF (80:10:10 wt%)	140.8 (C/10)	98 (5C)	92%/200 cycles (2C)	[66]
PEDOT:PSS (5 wt%)-C-LFP		PEDOT:PSS-C-LFP/CB/PVDF (80:10:10 wt%)	154.6 (C/10)	ca. 120 (5C)	96%/200 cycles (2C)	[66]
PANI:CSA (10 wt%)-C-LFP		PANI:CSA-C-LFP/CB/PVDF (70:20:10 wt%)	165.3 (C/10)	108.7 (5C)	ca. 97%/50 cycles (C/10)	[67]
PTPA (10 wt%)-C-LFP		PTPA-C-LFP/CB/PTFE (70:20:10 wt%)	154.5 (C/10)	114.2 (10C)	ca. 97%/50 cycles (C/10)	[68]
PANI (15 wt%)-C-LFP	Solvent-free mixing of $LiFePO_4$ and a polymer	PANI-C-LFP/CB/B (75:15:10 wt%)	164 (C/5)	130 (2C)	close to 100%/150 cycles (C/5)	[69]

3.2. EAECPs as Conductive Binders

Conductive carbon additives and binders are two components of an auxiliary carbon-binder network around $LiFePO_4$ particles. In this network, the carbon provides electrical conduction pathways from the current collector to the active material, and the binder ensures mechanical integrity and good electrical contact of the cathode through establishing cohesion between all active layer components and their adhesion to the current collector. Conventional carbon-binder networks possess several drawbacks such as carbon agglomeration, insulating nature of binders and their poor adhesion to electrode components, negligible capacity, which limit the overall cathode performance. Difficulties in achieving effective dispersion of conventional carbon additives and binders with $LiFePO_4$ particles in a wet mixing process is a challenge lead to structural bottlenecks that interrupt the electronic and ionic transport in within the electrode [19].

Electrochemically active polymers possess electronic conductivity, strong adhesive properties and non-negligible capacity so they have been suggested as a replacement (either complete or partial) for the conventional carbon-binder network [71]. In this section, various methods for incorporating EAECP conductive binders into the $LiFePO_4$-based cathodes as well as the compositions and structures of the resulting electrodes are summarized. Representative studies are summarized in Table 3. Two main scenarios include: (i) using EAECP as a single conductive binder ($LiFePO_4$/EAECP cathode configuration); (ii) using EAECP as a component of the conductive additive-binder network, i.e., in combination with another conductive additive ($LiFePO_4$/CA/EAECP), another binder ($LiFePO_4$/EAECP/B) or both ($LiFePO_4$/CA/EAECP/B). Different studies report different methods for the calculation of specific capacities of these composite cathodes: based on the mass of $LiFePO_4$ or based on the mass of the active layer. The latter approach seems to be more justified and will be used in the discussion that follows unless specified otherwise.

3.2.1. EAECPs as Single Conductive Binders

In this electrode configuration, the EAECP performs binding and conductive functions in the cathode and does not require the use of auxiliary conductive additives or binders. Several chemical and electrochemical synthetic strategies for the preparation of two-component $LiFePO_4$/EAECP active layers have been described.

$LiFePO_4$/EAECP Cathodes Prepared by Chemical Methods

The most widely used method involves mechanical mixing of ex situ synthesized EAECP and $LiFePO_4$ particles in a proper solvent; the slurry is then coated onto an aluminum current collector using doctor-blade or more elaborate techniques [72–81]. Composite electrodes containing both intrinsically conducting [72–80] and redox polymers [81] have been prepared using this approach.

Cíntora-Juárez et al. mixed electropolymerized PEDOT and active material (LFP or C-LFP) in N-methyl pyrrolidone (NMP) to form cathode slurry [73]. The resulting cathodes (LFP/PEDOT 80:20 and C-LFP/PEDOT 83:17) delivered similar discharge capacities at C/10 rate (115 mAh/g for LFP/PEDOT and 113 mAh/g for C-LFP/PEDOT), which was an improvement over respective baseline LFP(C-LFP)/CB/PVDF (85:8:7 wt%) cathodes. The C-LFP/PEDOT composite demonstrated better performance at 2C in comparison with LFP/PEDOT, which lost more than 50% of its low rate capacity and suffered considerable drop in potential at similar rate. The authors suggested that the improved performance of C-LFP/PEDOT at moderate C-rates could be attributed to better chemical affinity of the polymer for the carbon coating on the LFP surface than for bare LFP particles and to the formation of a more extended conducting polymer matrix in the former case. The proposed method requires the use of the same expensive and toxic organic solvent (NMP) that is used for the PVDF-containing electrode fabrication, which constitutes a certain disadvantage of the method.

A number of studies reported the cathode slurry preparation using EAECPs that could be processed in aqueous conditions. In general, the use of water as a solvent is cost-effective and environmentally benign, and the water-soluble polymers can be easily functionalized to enable target properties, such as for example, higher adhesion strength or faster Li^+ ions diffusion [82]. Several research groups described the preparation of $LiFePO_4$/EAECP composite layers using an aqueous dispersion of PEDOT:PSS [74,76–80]. Das et al. used commercially available PEDOT:PSS (1.3% dispersion in water) to obtain a series of two-component C-LFP/PEDOT:PSS electrodes containing 6 wt%, 8 wt%, and 16 wt% polymer and compared their performance with a conventional C-LFP/CB/PVDF cathode (84:10:6 wt%) [76]. They found that with increasing the amount of conductive polymer binder in the electrode, the carbon-coated $LiFePO_4$ particles became less agglomerated, the particle size distribution became narrower, but the cathode porosity decreased. As a result, 8 w% PEDOT/PSS was determined as the optimal amount of binder in the composite system. The respective electrode delivered the highest discharge capacity (about 120 mAh/g at C/5) and showed the highest rate capability out of all studied samples. It was also found that the mechanical, physical, morphological and electrochemical properties of C-LFP/PEDOT/PSS (92:8 wt%) cathode were affected by the solid loading of the slurry before coating [77]. The optimal electrochemical performance was achieved with the slurries containing 40% solid loading. Despite the high porosity and an increased amount of active material vs. the conventional formulation, the composite cathodes containing 6 wt% PEDOT/PSS showed reduced capacity, high overvoltages and poor rate capability due to low electronic conductivity [76]. Similar results were obtained by Raj et al. for C-LFP/PEDOT:PSS cathodes with different amounts of the polymer (3 wt%, 6 wt%, 9 wt% and 12 wt%) prepared from 3% aqueous PEDOT:PSS dispersion [80]. The optimal electrochemical performance was observed for the electrodes containing 9 wt% PEDOT:PSS whereas samples containing 3 wt% and 6 wt% polymer displayed poor performance due to inhomogeneous binder distribution and low conductivity. In contrast with those results [76,80], Levin et al. were able to utilize a commercial 1.3% aqueous dispersion of PEDOT:PSS to successfully prepare two-component $LiFePO_4$ electrodes with 99.5 wt% active material and only 0.5 wt% conductive binder [74]. These cathodes delivered discharge capacity of 147 mAh/g at C/5 (a 15% improvement over the conventional C-LFP/CB/PVDF (84:8:8 wt%) formulation), showed enhanced rate capability and good cycling stability. The authors thus showed that even at 0.5 wt% content, PEDOT:PSS could keep the mechanical integrity of the composite on the current collector and form enough conductive pathways between carbon-coated $LiFePO_4$ particles but they did not specify the thickness of the prepared active layer. Sandu et al. turned a commercial 1.3% aqueous PEDOT:PSS dispersion into a hydrogel by ball milling its mixture with LFP particles [79]. This way, more viscous and stable slurries were produced, which allowed easier processing and preparation of higher quality and defect-free electrodes that showed power-rate and cycling stability performances similar to the regularly processed solution-based formulations. Syrovy et al. utilized the in-house synthesized PEDOT:PSS aqueous dispersion to prepare ink formulation, where 18 g of $LiFePO_4$ was mixed with 100 g of PEDOT:PSS dispersion [78]. The ink, which also contained ethylene glycol and a gemini wetting agent, was used to screen print composite cathode layers onto an Al foil. A fully screen printed C-LFP/PEDOT-PSS cathode showed enhanced discharge capacity (151.2 mAh/g at C/2), higher conductivity and stability under cycling tests in comparison to the screen printed C-LFP/CB/PVDF baseline electrode.

Several studies demonstrated the use of EAECPs exhibiting both electronic and enhanced ionic conductivity as single conductive binders in $LiFePO_4$ cathodes. Javier et al. synthesized a poly(3-hexylthiophene)-*b*-poly(ethylene oxide) (P3HT-PEO) block copolymer in which the conjugated P3HT segments were responsible for potential-dependent electronic conductivity and PEO fragments provided lithium ion conduction [72]. The composite C-LFP/P3HT-PEO cathode (50:50 wt%) was able to operate in an all-solid state battery showing a specific capacity of about 140 mAh/g at C/4 (the authors did not specify if this number was referred to the total mass of the composite electrode or, more likely, the $LiFePO_4$ mass). The P3HT-PEO itself demonstrated electrochemical activity during the charge–discharge cycling but its capacity was less than 10 mAh/g of polymer so it was not considered by the authors of this study. Ling et al. carried out the synthesis of SA-PProDOT polymer from sodium algenate (SA) and 3,4-propylenedioxythiophene-2,5-dicarboxylic acid (ProDOT) (Figure 4) [75]. The polymer demonstrated sufficiently high electronic (due to the conjugated structure) and ionic (due to the SA component) conductivity to enable $LiFePO_4$ material to deliver its theoretical capacity of ca. 170 mAh/g (based on the active mass of LFP) in the first charge–discharge cycle of LFP/SA-PProDOT electrode (80:20 wt%) at C/10 and maintain ca. 120 mAh/g at 1C for more than 400 cycles. Excellent binding properties of SA-PProDOT assisted in improved mechanical stability and adhesion among the active layer, current collector, and LFP particles.

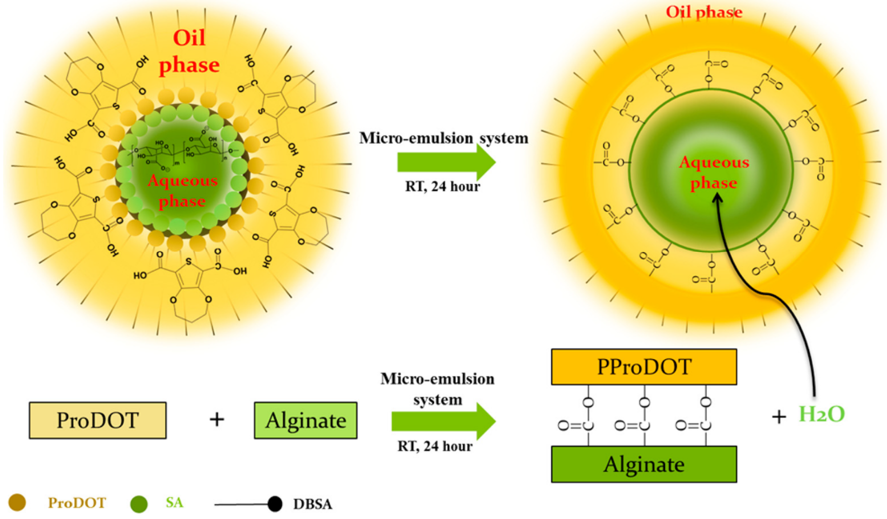

Figure 4. Schematic design of the microemulsion system for synthesis of SA-PProDOT polymer. SA and ProDOT molecules self-assemble along with hydrophilicity of the functional groups, forming an interface where the esterification reaction takes place. The produced water is removed from the interface to the hydrophilic phase, which advances the reaction equilibrium forward [75]. Reprint with permission from [75]; Copyright 2015, American Chemical Society.

Wang et al. designed a novel redox polymer binder containing poly (4-vinylpyridine) and phenoxazine moieties tethered with a C_{12} alkyl chains (poly(4-((10-(12-dodecyl phenoxazine)vinyl pyridinium)-co-4-vinylpyridine) (bis(trifluoromethanesulfonyl) imide)–PVP-DD-PXZ 6/1 (6:1 molar ratio of pyridine to phenoxazine)) and used it to make cathodes from virtually non-conductive carbon-free $LiFePO_4$ in a proof-of-concept study [81]. In an LFP/PVP-DD-PXZ (9:1 wt%) cathode, the redox polymer operated according to the "polymer wiring" mechanism that involved oxidation of tethered "swing" PXZ moieties to PXZ^+ at the current collector, followed by delivering the positive charge to the $LiFePO_4$ particles via intermolecular hopping assisted by motion of the shuttle moiety (Figure 5). The obtained charge–discharge curves indicated that the insulating $LiFePO_4$ material participated in the electrochemical processes in the active layer but fast capacity decay was observed. Nevertheless, the polymer wiring concept was proved viable.

The approach to the preparation a two-component LFP/EAECP electrode developed by Shi et al. also involved making $LiFePO_4$-based slurry but instead of using a pre-synthesized EAECP as the second slurry component, the polymer (a cross-linked polypyrrole (C-PPy)) was chemically synthesized in situ by adding pyrrole monomers, cross-linkers and an oxidant to C-LFP particles in an aqueous dispersion (Figure 6) [83]. The resulting slurry was coated onto Al foil; the polymerization inside the coated layer continued overnight to yield nanostructured polymer gel with embedded C-LFP particles. The authors found that by being highly conductive, hierarchically porous, chemically stable, mechanically flexible and robust, C-PPy gel framework promoted electron and ion diffusion in the composite layer, facilitated the uniform distribution of active material and prevented its aggregation in the composite layer. As a result, the in situ manufactured C-LFP/C-PPy cathode (85:15 wt%) delivered a specific capacity of ∼150 mAh/g at C/2 (a clear improvement over a conventional C-LFP/CB/PVDF electrode (85:10:5 wt%), which showed only ∼130 mAh/g at the same discharge rate) and exhibited greatly improved rate and cyclic performance. The capacity of C-PPy in the applied voltage range was only ~15 mAh/g, which made its contribution to the total electrode capacity negligible.

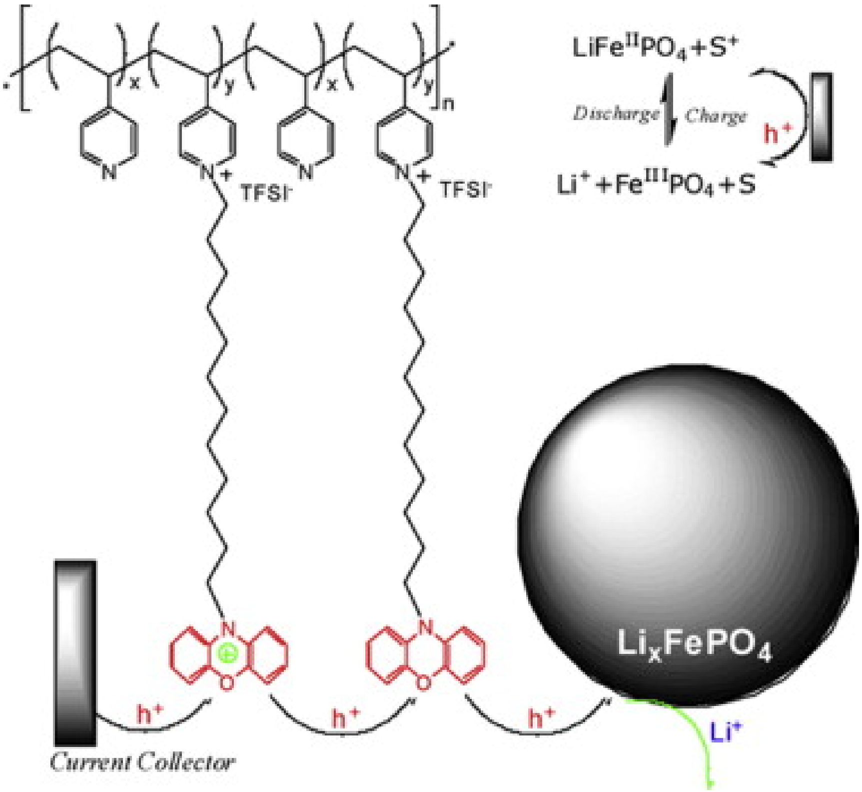

Figure 5. Schematic model showing the working principle of polymer wiring of insulating electrode materials. Here, carbon-free $LiFePO_4$ was studied with redox polymer poly(4-((10-(12-dodecyl phenoxazine) vinylpyridinium)-co-4-vinylpyridine) in a molar ratio of 6:1 ($y/x = 5$) [81]. Reprint with permission from [81]; Copyright 2009, Elsevier.

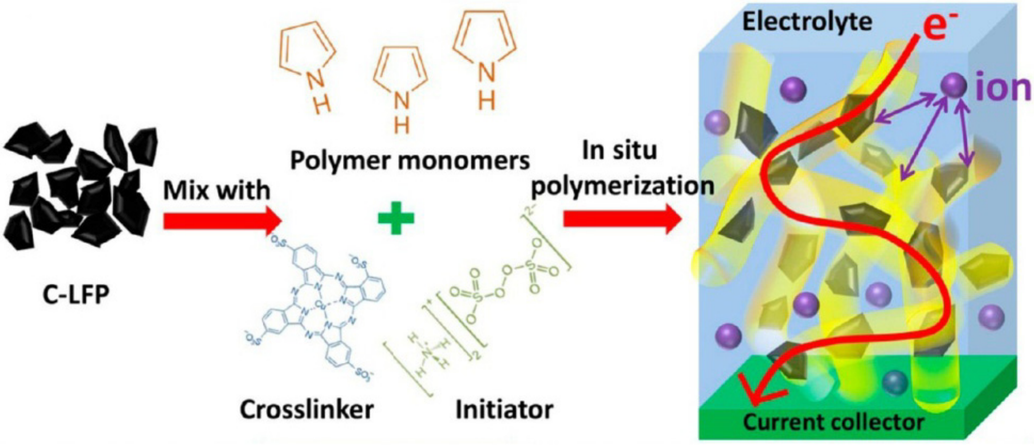

Figure 6. Schematic of synthetic and structural features of C-LFP/C-PPy hybrid gel framework [83]. Reprint with permission from [83]; Copyright 2017, American Chemical Society.

The discussed methods for the preparation of two-component composite $LiFePO_4$/EAECP cathodes are attractive in terms of simplicity, scalability, and active layer composition control as they essentially involve mixing of two components to form a slurry, which is then cast onto a current collector. However, as any mixing procedure, it can be sensitive to the process conditions and require precise control over electrode morphology to prevent undesired particles agglomeration and increased interfacial charge transfer resistance.

$LiFePO_4$/EAECP Cathodes Prepared by Electrochemical Methods

Electrochemical methods for the fabrication of two-component $LiFePO_4$/EAECP composite films involve in situ electrochemical polymerization of corresponding monomers in the presence of lithium iron phosphate particles. These techniques allow the preparation of three-dimensional cathode frameworks with an extended web-like EAECP matrix, maximized contact area and minimized contact resistance between the polymer and the embedded $LiFePO_4$ particles. Both current collector-supported [40,84–87] and free-standing [88,89] $LiFePO_4$/EAECP composites have been synthesized by these methods.

The in situ electrodeposition technique for fabrication of $LiFePO_4$/EAECP layers on the current collector surface was developed by the Goodenough research group [40,84–86]. The method involved co-deposition of active material particles and the polymer matrix onto the working electrode (current collector) during electropolymerization of the monomer in the non-aqueous electrolyte suspension of C-LFP powder. The authors used this method to prepare C-LFP/PPy composite films by conducting the electrodeposition in cyclic voltammetry [40,84–86] or consecutive potential steps conditions [86]. The latter technique was found to allow better control of the polymerization potential and time and hence more precise management of the growth and morphology of the polymer. The success of the composite cathode fabrication by in situ electrodeposition was shown to largely depend on two factors: (a) the presence of carbon coating on the lithium iron phosphate particles (the coating promotes bonding of the PPy to the $LiFePO_4$ particles, which provides good electronic contact between the oxide particles and the current collector) [85]; (b) the overlap of the electroactive range of the polymer and C-LFP [40]. Composites with different percentage of PPy (up to 32 wt% [86]) were prepared. The highest discharge capacity was observed for the C-LFP/PPy (80:20 wt%) electrode electrodeposited in potential steps conditions: 154 mAh/g at C/10 (a 20%improvement over a conventional C-LFP/CB/PVDF (80:11:9 wt%) layer). The enhancement of the specific capacity of the composite was partially assigned to the contribution of the polymeric material to the charge-storage capacity (the specific capacity of PPy was determined as 90 mAh/g) [86]. Composite C-LFP/PPy cathodes also exhibited enhanced rate capability and stable cycling [40,84–86].

Later, Polozhentseva et al. used the electrochemical co-deposition method to produce two-component composite cathodes containing C-LFP particles dispersed in a conducting metallopolymer matrix synthesized from nickel(II) complexes with Salen type ligands [87]. The monomeric complexes were electropolymerized by applying oxidative potential steps to the carbon-coated aluminum foil immersed in the monomer solution containing dispersed C-LFP particles. The resulting composite electrodes were not optimized in terms of the percentage of the polymer in the composite so their specific capacity did not exceed 137 mAh/g at C/10, which was lower than the baseline electrode capacity (139 mAh/g for C-LFP/CB/PVDF (90:5:5 wt%)), but the composites showed better rate capability and similar cycling stability versus the baseline. The authors found that $\sim$10% of the composite cathode capacity came from the polymer matrix, which performed conductive, binding, and energy storage functions in the system.

The possibility of obtaining free-standing $LiFePO_4$/EAECP films and using them as cathodes in Li-ion cells was demonstrated by Wang et al. [88]. The authors produced $LiFePO_4$/PPy layers on a polished stainless steel plate by using galvanostatic mode of electrodeposition in the electrolyte containing dissolved pyrrole and ultrasonically dispersed LFP powder. The resultant films were peeled off from the support and used directly as cathodes in electrochemical characterization tests. Their discharge capacity was quite low

(80 mAh/g), probably due to the low amount of LFP in the composite (38 wt%) but the charge and discharge curves displayed plateaus characteristic of the $Fe^{2+}/^{3+}$ redox couple in the $LiFePO_4$, which confirmed the ability of the conductive binder to support the Li^+ ion extraction and insertion in the active material in the absence of a current collector. The authors considered the obtained results preliminary, and yet, useful in light of growing market demand for flexible and bendable batteries. Trinh et al. prepared free-standing $LiFePO_4$/PEDOT composite films by dynamic three phase interline electropolymerization (D3PIE) [89]. The method consisted in immersing the electrode through the interface of a biphasic system, in which the aqueous phase contained BF_4^- doping ions and C-LFP powder and the organic phase contained EDOT monomers, and subjecting the electrode to an oxidative overpotential. As a result, the PEDOT polymer grew along the interface while simultaneously incorporating C-LFP particles (Figure 7). The synthesized film was easily removed from the reaction media and used without further modification as the cathode in standard lithium ion batteries. The potential-dependent electronic conductivity of PEDOT remained sufficiently high in the operating voltage of $LiFePO_4$ to support the battery charge and discharge. The composite contained only 33.5 wt% C-LFP, so it discharged only 75 mAh/g at C/10, which however corresponded to quite high discharge capacity of ~160 mAh/g when calculated based on the amount of $LiFePO_4$ in the film. The authors also showed that the specific capacity of their free-standing cathode was similar to that of a conventional electrode containing 80-90 wt% active material if the mass of the current collector was included in the calculations. In a different study [73], the LFP/PEDOT and C-LFP/PEDOT composites prepared by D3PIE method were grinded and then dispersed in NMP for coating onto the current collector. The resulting electrodes showed rather poor performance, which highlights the importance of preserving the three-dimensional PEDOT network for effective electronic conduction.

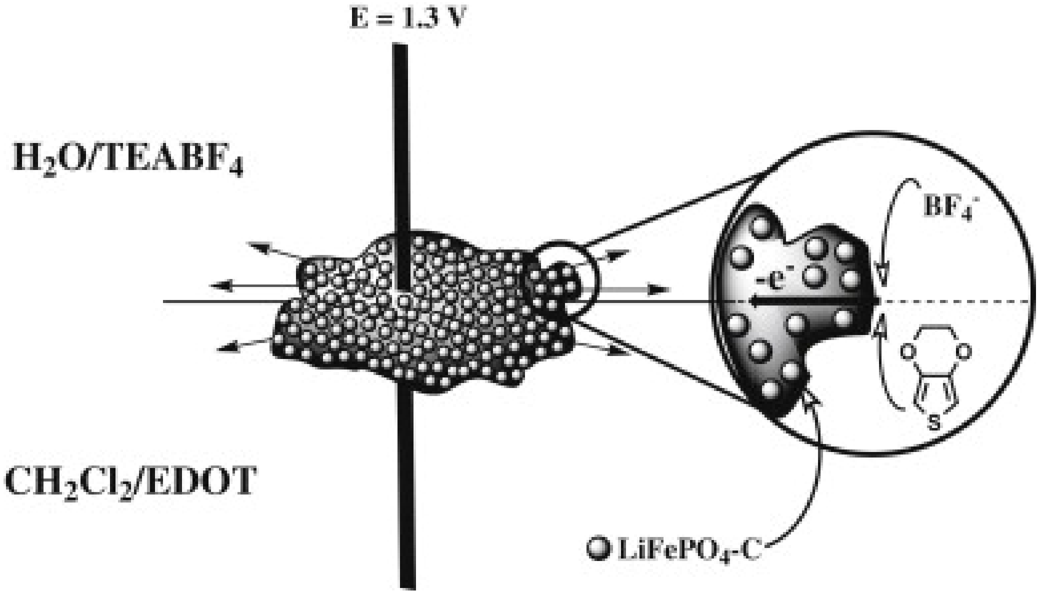

Figure 7. Schema of the D3PIE method in dynamic growth with $LiFePO_4$ at the water/dichloromethane interface [89]. Reprint with permission from [89]; Copyright 2013, Elsevier.

Electrochemical methods allow to form a continuous EAECP matrix that binds finely dispersed lithium iron phosphate particles into a mechanically robust and flexible three-dimensional electron/ion conducting network with minimized interfacial charge transfer resistance and improved electric contact between $LiFePO_4$ particles and the current collector. Electrochemical techniques provide the unique opportunity to manufacture free-standing active layers that do not require a current collector (thus, the electrode capacity can be further improved). At the same time, it appears that this approach does not allow to deposit active layers with high inorganic phase content, which limits the attainable specific capacity values of produced materials. Together with scalability issues, this presents serious disadvantage of the discussed electrochemical deposition techniques.

3.2.2. EAECPs as Components of Conductive Additive-Binder Networks

Two-component $LiFePO_4$/EAECP composites appear to be the most advantageous cathode formulations as they eliminate the use of all “dead weight and volume” auxiliary components. However, excellent electronic and ionic conductivity, adhesion strength, non-negligible specific capacity, decent mechanical, chemical, and electrochemical stability as well as good processability required for target electrode performance are rarely found in one EAECP. As a result, various auxiliary components are added to the active layer to compensate for the relative weaknesses of the polymeric conductive binders.

$LiFePO_4$/CA/EAECP Cathodes

In this type of composite electrodes, an auxiliary conductive additive (carbon black [90–94], single wall carbon nanotubes (SWCNTs) [80,95,96] or multi-wall carbon nanotubes (MWCNTs) [94] is used in the electrode formulation to improve electron pathways between EAECP domains, lithium iron phosphate particles and the current collector. The addition of a CA is supposed to facilitate high rate performance of the composite cathode if the polymer displays limited electronic conductivity. $LiFePO_4$/CA/EAECP composite electrodes are usually produced by coating the current collector with slurries made by mixing $LiFePO_4$ particles, ex situ synthesized polymer, and a conductive additive.

Tamura et al. prepared C-LFP/CB/PANI (85:9:6 wt%) electrodes using commercially available carbon-coated lithium iron phosphate, acetylene black, and in-house synthesized PANI prepared by the chemical oxidation of aniline [90]. The composite film (Figure 8) showed improved adhesion to the Al current collector, smaller polarization during charge–discharge, enhanced rate capability and higher specific capacity (132 mAh/g at 1C) compared to the conventional C-LFP/CB/PVDF (85:9:6 wt%) layer (119 mAh/g at 1C). The authors estimated the capacity added due to the redox of PANI was only 6 mAh/g composite and concluded that the utilization of the active material ($LiFePO_4$) was increased by using PANI as a binder. The improved performance of the composite cathode was also attributed to the intimate contact between C-LFP particles and highly conductive doped PANI, which was effective in decreasing the electrode resistance.

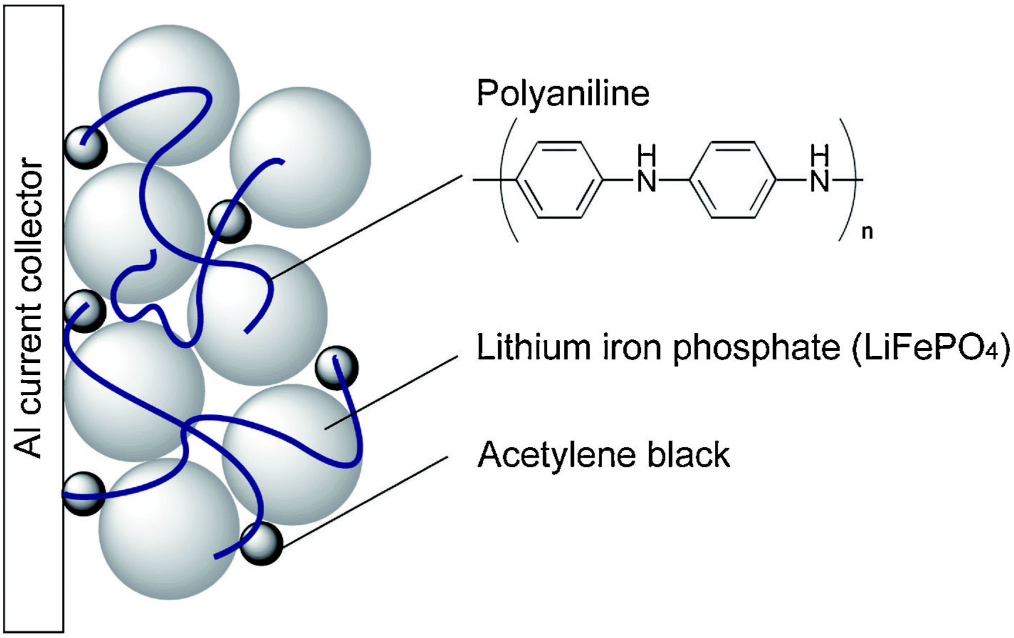

Figure 8. Schematic illustration of the composite polyaniline/ $LiFePO_4$ cathode [90]. Reprint with permission from [90]; Copyright 2011, The Chemical Society of Japan.

Ranque et al. used a small amount of carbon black (2 wt%) to prepare $LiFePO_4$–based electrodes using a novel redox active multifunctional binder based on a polyacrylate bearing perylene diimide moieties in the side chain (PPDI)[91]. The developed composite layers containing 18 wt% of PPDI delivered similar performance to the $LiFePO_4$ cathode of standard formulation ($LiFePO_4$/CB/PVDF (80:10:10 wt%)) and significantly higher capacity and cyclability compared to the conventional electrode containing the same amounts of CB (2 wt%) and binder (18 wt% PVDF). The authors suggested that the electrochemical activity (~50 mAh/g practical capacity) and stability of PPDI over the operating voltage range of $LiFePO_4$ cathode were critical to improving battery performance.

The addition of carbon black to the slurry formulation during the fabrication of $LiFePO_4$-based cathodes with a multifunctional PEDOT-PSS binder was demonstrated in several studies [92–94]. Eliseeva et al. produced C-LFP/CB/PEDOT:PSS (92:4:4 wt%) cathodes using commercially available materials: carbon-coated lithium iron phosphate, 1.3 wt% dispersion of PEDOT:PSS in water and conductive carbon black [92,93]. The composite electrodes showed high discharge capacities of 147 mAh/g [93] or 165 mAh/g [92] at C/5 (the difference in electrode performance could possibly originate from the undisclosed differences in the preparation procedure or material loading) and very good rate capability up to 5C. The authors showed that the addition of carbon black to the C-LFP/PEDOT:PSS composite formulation yielded enhanced charge transport in the cathode layers [93]. Similar results were obtained by Raj et al. who used carbon-coated $LiFePO_4$ synthesized by sol-gel method, carbon black, and 3 wt% aqueous PEDOT:PSS dispersion to prepare electrodes with ∼9 wt% CB additive and different polymer content (3 wt%, 6 wt%, 9 wt%, and 12 wt%) [94]. All electrodes showed enhanced electrochemical performance over C-LFP/PEDOT:PSS cathodes containing the same amounts of the polymeric conductive binder, especially at 2C and 5C discharge rates [80].

Even more impressive performance was observed for the C-LFP/CA/PEDOT:PSS composite cathodes that utilized carbon nanotubes as an auxiliary conductive agent. Raj et al. [80] and Kubarkov et al. [95] independently described the preparation of the composites using SWCNTs as electronic conduction-promoting additives. In both studies, the carbon-coated LFP material was synthesized in the lab. Raj et al. used commercial 3% aqueous PEDOT:PSS dispersion and 5–30 µm long SWCNTs whereas Kubarkov et al. employed in-house polymerized PEDOT:PSS and >5 µm long SWCNTs. Both research groups obtained composite electrodes able to perform at very high rates (up to 20C [95] or 100C [80]). The C-LFP/SWCNT/PEDOT:PSS (~82:9:9 wt%) cathode prepared by Raj et al. delivered discharge capacity of 166.6 mAh/g at C/10 rate, which was almost equivalent to theoretical capacity of $LiFePO_4$ [80]. Such enhanced composite electrode performance was explained by the synergistic effect of SWCNTs and PEDOT:PSS resulting in the high conductivity of the cathode active layers due to high electron mobility in SWCNTs in composite and charge domains dispersed in conducting PEDOT:PSS polymer. The formation of efficient conductive paths in the electrode composite was related to the π-π interactions between the conjugated structure of PEDOT and the π-electronic SWCNT surface, which provided an improved junction of the C-LFP particles with the conductive SWCNT network in the composite cathode [95]. Unfortunately, according to Kubarkov et al., C-LFP/SWCNT/PEDOT:PSS (95:0.25: 4.75 wt%) layer showed rather poor adhesion to the aluminum foil current collector, which resulted in poor cycling stability of the composite cathode (~25% capacity fade after 150 cycles at 1C) [95]. A synergistic effect was also discovered for the MWCNT and PEDOT:PSS combination as it was utilized for the preparation of $LiFePO_4$-based composite cathodes [94]. In a comparative study, MWCNTs used as an auxiliary conductive additive provided significantly greater improvement in the discharge capacity and rate capability of C-LFP/CA/PEDOT:PSS cathodes than carbon black [94].

Hatakeyama Sato et al. used SWNTs as a conductive additive to prepare a composite electrode from $LiFePO_4$ and redox polymer poly(TEMPO-substituted glycidyl ether) with ethylene oxide units introduced in the side chains (P2b) [96]. In the prepared $LiFePO_4$/SWCNT/P2b (70:10:20 wt%) sample, P2b polymer performed not only as an electron/ion conductor and a binder possessing charge storage properties but also as an oxidative mediator undergoing fast oxidation to form oxoammonium cations during the charging process. These cations functioned as the oxidants to $LiFePO_4$ particles. The charge mediation enabled the composite cathode to deliver a specific charging capacity of 70 mAh/g at 50C while only 38 mAh/g was obtained with the pristine $LiFePO_4$/SWCNT (90:10 wt%) sample at the same rate.

It appears that the use of even small amounts of auxiliary conductive additives represents a powerful tool to boosting the electronic conductivity of the composite $LiFePO_4$/EAECP cathodes. The best results were obtained for carbon nanotubes, which have a large aspect ratio and an open porous structure in comparison with standard carbon additives. At the same time, achieving good dispersion stability of carbon nanotubes in the cathodic slurry can be challenging, and cost considerations can be regarded as a limiting factor in the implementation of the proposed solutions.

$LiFePO_4$/EAECP/B Cathodes

In this type of composite cathodes, an auxiliary binder (PVDF [97–99], carboxymethyl cellulose (CMC) [93,100], poly(ethylene oxide) (PEO) or sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) [101] is added to the electrode formulation to improve ionic conductivity and/or mechanical integrity of the electrode. The cathodes of this type are usually prepared from slurries containing three active layer components (LFP, ex situ synthesized EAECP, and binder) [93,97,98,100,101] but an alternative technique for electrode fabrication has also been described [99].

Wijayati et al. [97] and Rahayu et al. [98] attempted to prepare $LiFePO_4$-based cathodes with PANI synthesized by interfacial polymerization method and used a conventional PVDF binder as an additional electrode component to improve mechanical properties of the cathode. Wijayati et al. reported that the electrical conductivity of the composite layer containing 8 wt% PVDF improved by two-fold when the PANI content was increased from 0 to 10 wt% [97]. Rahayu et al. found that the discharge capacity of the prepared $LiFePO_4$/PANI/PVDF (70:15:15 wt%) cathode was only 38 mAh/g and suggested that the low active material unitization could be due to high percentage of non-conductive PVDF in the composite [98].

$LiFePO_4$-based cathodes containing PEDOT:PSS as a conductive binder and ion-conducting polymer as an additional binder have been described in several studies. Eliseeva et al. used CMC as an auxiliary binder in C-LFP/PEDOT:PSS/CMC cathodes (96:2:2 wt%) [93,100]. CMC is an aqueous binder so it is more compatible with an aqueous PEDOT:PSS dispersion used for the slurry preparation than a conventional PVDF binder. As an ion conductor and a thickening agent, it could facilitate processability, mechanical properties, and conductivity of the composite cathode. Eliseeva et al. demonstrated high discharge capacity of the composite electrodes (148 mAh/g active layer, 154 mAh/g LFP at C/5) assigned to high utilization of LFP in the presence of the PEDOT:PSS/CMC composite conductive binder and partly to additional contribution of the PEDOT:PSS redox [100]. The electrode also showed good rate capability in the range C/5–1C but diminished performance at higher discharge rates, which was indicative of insufficient conductivity of the composite cathode without the use of any auxiliary conductive additives [93]. Kubarkov et al. demonstrated that the addition of PEO or SPPO as co-binders to the PEDOT:PSS-based formulations afforded the preparation of both thin (20 μm) and fairly thick (>50 μm) C-LFP/PEDOT:PSS/B active layers with high areal capacity [101]; the latter was difficult to achieve in two-component C-LFP/PEDOT:PSS electrodes [76]. The prepared C-LFP/PEDOT:PSS/SPPO (95:2.5:2.5 wt%) and C-LFP/PEDOT:PSS/PEO (95:3:2 wt%) cathodes exhibited higher specific capacity (154 mAh/g $LiFePO_4$ and 151 mAh/g $LiFePO_4$ at C/10, respectively) compared to the conventional C-LFP/SP/PVDF (95:2.5:2.5 wt%) electrode (∼138 mAh/g $LiFePO_4$ at C/10), which was attributed by the authors to good film-forming and adhesive properties of SPPO and PEO and hence improved utilization of the active material capacity, rather than to possible differences in electrical conductivity of PEDOT:PSS- and PVDF-based formulations. Both PEDOT:PSS/polymer binders improved rate performance comparing to traditional cathode composition. Unlike PEO, which was insoluble in conventional carbonate electrolytes, SPPO co-binder was compatible with carbonates, which allowed the C-LFP/PEDOT:PSS/SPPO cathode to also show high stability and cyclabilty.

An alternative in situ technique for the fabrication of $LiFePO_4$/EAECP/B cathodes was developed by O'Meara et al. [99]. They prepared a slurry containing carbon-coated $LiFePO_4$, PVDF, and a monomeric nickel(II) complex with a salen-type ligand [Ni(CH_3-salen)], cast it onto a carbon-coated aluminum foil, assembled such obtained electrodes in lithium half-cells, and galvanostatically charged the cells to 4.3 V at C/10, which caused the monomers to polymerize in the bulk and on the surface of the cathode. In the in situ polymerized C-LFP/poly-[Ni(CH_3-salen)]/PVDF (93:5.5:1.5 wt%) electrode, the polymer component played several positive roles (Figure 9), which afforded promising battery performances that surpassed the conventional C-LFP/CB/PVDF (90:5:5 wt%) electrodes. More specifically, the composite cathodes discharged 142 mAh/g at C/10 (132 mAh/g for a conventional sample), which translated to 153 mAh/g $LiFePO_4$ (147 mAh/g for a conventional electrode). The improvement was found to result from additional redox from poly-[Ni(CH_3-salen)] and increased utilization of $LiFePO_4$. The composite cathodes also showed improved rate capabilities at C/10–5C attributed to facilitated charge transfer across large contact area polymer/C-LFP interfaces. The enhanced cyclability of the composite electrodes compared with that of the conventional counterparts was related to higher mechanical integrity of the former and less intensive electrode/electrolyte interfacial side reactions at the polymer-coated layer of C-LFP.

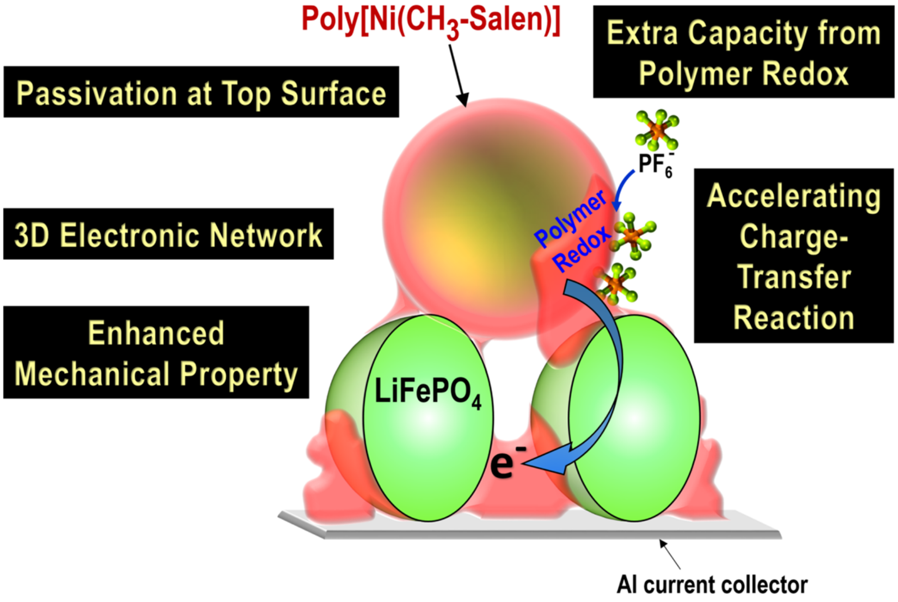

Figure 9. Multiple Roles of Poly[Ni(CH_3-Salen)] in Carbon-Free Cathodes: (i) formation of 3D electronic network, (ii) accelerate charge-transfer reaction of cathode, (iii) providing extra capacity from the redox of poly[Ni(CH3-salen)], thus increasing energy density at cathode level, (iv) enhanced mechanical property as a binder for cathodes, and (v) passivation of active materials at top surface. The direction of electrochemical reactions is for a battery-charging process [99]. Reprint with permission from [99]. Copyright 2019, American Chemical Society.

Out of all proposed $LiFePO_4$/EAECP/B cathode designs and manufacturing techniques, the use of ionically conducting binders appears as an attractive approach to boosting the electrode performance, in addition to enhancing the mechanical properties of the active layers. The in situ manufacturing technique proposed in [99] combines the advantages of electrochemical and slurry casting procedures, and could potentially be used with other polymer chemistries. However, as in the case of additional conductive additives, the use of a second binder is a step back from the objective of fully replacing all "dead weight" components with EAECPs in the cathode active layer.

$LiFePO_4$/CA/EAECP/B Cathodes

In this type of electrodes, auxiliary conductive additives and binders are both added to the electrode formulation, although in reduced amounts versus conventional electrodes. Basically, this is a combination of the above described approaches ($LiFePO_4$/CA/EAECP and $LiFePO_4$/EAECP/B) so the utilized conductive additives, binders, and electrode fabrication methods are quite similar to the ones used for the preparation of three-component composite electrodes.

In a number of studies, $LiFePO_4$-based cathodes were prepared using conventional additives (carbon black and PVDF) to the slurry containing lithium iron phosphate and ex situ polymerized EAECP (PEDOT:PSS [102,103], poly-o-methoxyaniline [104], PANI [105], or a redox active fluoflavin polymer [106]). Cíntora-Juárez et al. [102] reported the fabrication of two different $LiFePO_4$/CB/PEDOT:PSS/PVDF electrodes (79:7:7:7 wt% and 84:8:1:7 wt%) from in-house synthesized lithium iron phosphate and a commercial PEDOT:PSS aqueous dispersion (1.1 wt%). The authors found that the incorporation of PEDOT:PSS additives within the bulk of $LiFePO_4$ electrodes provided a three-dimensional, mixed conducting network that notably improved their performance. The addition of 7 wt% PEDOT:PSS to the electrode formulation had beneficial impact on the discharge voltage of the cathode but did not significantly influence the electrode capacity at C/10–5C compared to the conventional $LiFePO_4$/CB/PVDF (85:8:7 wt%) samples. A small amount (1 wt%) of PEDOT:PSS added to the electrode afforded a substantial improvement in the electrode capacity up to ~153 mAh/g LFP at C/10 and ~132 mAh/g LFP at 2C and a boost in the electrode performance at high rates thus indicating that PEDOT:PSS network promoted the ionic and electronic wiring of the LFP particles, including their contact to the current collector. Vicente et al. showed that adding PEDOT:PSS to the LFP/CB/PVDF electrode formulation during slurry preparation was more effective in reducing cathode resistance than coating LFP particle with conductive carbon [103]. Specific capacity of 130 mAh/g LFP at 2C was obtained for the PEDOT:PSS-containing electrode. The authors also found that the electrode preparation method was critical for the battery operation: drop casting PEDOT:PSS over a pre-formed LFP/CB/PVDF sample had detrimental effect on the electrochemical performance of the cathode.

Partial replacement of a conventional carbon-binder network in a C-LFP/CB/PVDF (84:10:6 wt%) formulation with poly-o-methoxyaniline (POMA) allowed Das et al. to prepare C-LFP/CB/POMA/PVDF (84:10:4:2 wt%) cathodes with 15% higher specific capacity (145 mAh/g $LiFePO_4$) in comparison to the conventional sample (126 mAh/g $LiFePO_4$), which was attributed to both POMA redox and improved utilization of active material [104]. At the same time, the composite electrode failed to demonstrate good high rate performance, likely because of the variable potential-dependent conductivity of the POMA. Another study reported the use of ex situ lithium-doped PANI as a conductive binder in $LiFePO_4$/CB/Li-PANI/PVDF composites [105]. The lithiation accomplished by treating PANI with n-butyllithium yielded enhanced crystallinity/order in Li substituted samples compared to pure PANI. The cells with composite cathodes demonstrated charge efficiency of around 98% and stable cycling performance over 50 cycles but low discharge capacity at C/10 ($\sim$40 mAh/g or lower, depending on the polymer lithiation level) because of very high Li-PANI content (around 90 wt%).

Composite $LiFePO_4$/CB/EAECP/PVDF electrodes containing a very low (catalytic) amount of the conductive polymer binder have also been described. Hatakeyama-Sato et al. added only 0.1 wt% nonconjugated redox-active polymer consisting of a polynorbornene backbone and fluoflavin pendant groups (FP) to a conventional cathode slurry to obtain a C-LFP/CB/FP/PVDF (89.9:2:0.1:8 wt%) composite cathode showing drastically improved performance over the standard C-LFP/CB/PVDF (90:2:8 wt%) sample, especially at high charge–discharge rates [106]. In particular, both electrodes exhibited discharge capacity of around 150 mAh/g $LiFePO_4$ at C/2 but the fluoflavin polymer-containing electrode was able to discharge 65 mAh/g $LiFePO_4$ at 30C whereas the baseline electrode delivered only 45 mAh/g $LiFePO_4$. The cyclability of the composite electrode was also enhanced. The authors attributed the observed performance improvement to the facilitation the electron injection/ejection of the inorganic material via redox mediation by FP, which possessed redox potential compatibility with lithium iron phosphate and insolubility in the battery electrolyte.

Some studies demonstrated the use of alternative binders (CMC [93,100,104,107], carboxylmethyl chitosan (CCTS) [108], and styrene-butadiene rubber (SBR) [109]) in combination with carbon black as slurry additives in the preparation of EAECP-containing $LiFePO_4$ cathodes. Eliseeva et al. reported the successful preparation of two C-LFP/CB/PEDOT:PSS/CMC composites with different component ratios (94:2:2:2 wt% [100] and 92:4:2:2 wt% [93]). While the electrochemical performance of the cathode containing 2 wt% carbon black additive was overall inferior to that of a C-LFP/PEDOT:PSS/CMC (96:2:2 wt%) electrode reported in the same study [100], adding higher amount (4 wt%) of conductive carbon to the slurry yielded a better performing composite electrode [93]. The C-LFP/CB/PEDOT:PSS/CMC (92:4:2:2 wt%) cathode showed discharge capacity of 148 mAh/g active layer at C/5, which was similar to the capacity of a C-LFP/PEDOT:PSS/CMC (96:2:2 wt%) electrode reported earlier by the same research group [100]. That was an indication that an optimum amount of auxiliary carbon additive helped improve the $LiFePO_4$ utilization in a C-LFP/PEDOT:PSS-based composite. The C-LFP/CB/PEDOT:PSS/CMC (92:4:2:2 wt%) cathode delivered similar performance to the three-component C-LFP/CB/PEDOT:PSS (92:4:4 wt%) electrode but had processability and cost advantages [93].

To improve the adhesive properties of PEDOT: PSS, it was also mixed with CCTS, and this 2-component binder was used to prepare $LiFePO_4$-based cathodes, which also contained carbon black and another auxiliary binder, SBR [108]. The resulting electrode delivered enhanced cycling and rate performances over the conventional sample. The authors found that PEDOT:PSS/CCTS favored the formation of continuous and homogenous conducting bridges throughout the electrode and increased the compaction density of electrode by reducing the carbon black content.

The four-component $LiFePO_4$/CA/PANI/SBR cathodes were prepared by Han et al. using different types of PANI, out of which the reduced PANI (r-PANI) enabled the most enhanced performance: the $LiFePO_4$/r-PANI-based composite cathode showed improved cyclability, rate capability, and ~4% higher specific capacity (154 mAh/g (based on the total mass of $LiFePO_4$ and r-PANI)) compared to the pure $LiFePO_4$-based electrode [109]. The performance improvement was related to the dual role of r-PANI as an active substance and a conductive agent forming a three-dimensional conductive network around lithium iron phosphate particles.

Das et al. prepared a C-LFP/CB/PEDOT:p-Tos/CMC (84:10:5.5:0.5 wt%) cathode containing highly conductive *p*-toluene sulfonate (p-Tos)-doped PEDOT as a multifunctional binder and tested it against the conventional C-LFP/CB/PVDF (84:10:6 wt%) sample [104]. Despite PEDOT:p-Tos did not demonstrate any electrochemical activity, it remained in conductive p-doped state in the potential range of the cathode functioning (2.5 to 4 V), so the composite electrode showed an improved capacity of 140 mAh/g $LiFePO_4$ (11% higher than the baseline) at C/5 and better rate capability in the range C/5–5C. Enhanced performance was attributed to the improved utilization of active material in the presence of a conductive polymer and possibly more advantageous electrode architecture.

An interesting example of a four-component composite cathode was demonstrated by Vlad et al. who hybridized $LiFePO_4$ and highly capacitive (111 mAh/g) redox polymer poly(2,2,6,6-tetramethyl-1-piperinidyloxy-4-yl methacrylate) (PTMA) in one electrode and added carbon black as a conductive agent and CMC as a binder [107]. Compositions with different capacity ratios of active materials C-LFP and redox polymer (1:1, 2:1, 4:1) were prepared. In the constructed composite C-LFP/PTMA-based electrode, the redox polymer was found to operate as an oxidative mediator for $LiFePO_4$ to accelerate the charging reactions. Due to the redox synergy of $LiFePO_4$ and PTMA, the composite electrodes outperformed both the pure C-LFP-based cathode and the pure PTMA-based cathode in terms of rate capability and specific capacity, respectively. They also showed improved cycling stability (more than 1500 cycles at 5C for the 1:1 composition) and enhanced safety during rapid recharge (Figure 10). The C-LFP/CB/PTMA/CMC layers showed an increase in the specific capacity (from 126 mAh/g actives for the 1:1 cathode to 150 mAh/g actives for the 4:1 cathode) and a decrease in the rate performance when more C-LFP was incorporated into the electrode, which prompted the authors to conclude that the power and energy density of the hybrid electrode could be precisely balanced by the respective amount of constituents, to fulfill the targeted application requirements. A similar case of redox mediation of $LiFePO_4$ charging by the adjacent hyperbranched poly(triphenylamine) (PHTPA) redox polymer binder was demonstrated by Yamamoto et al. for the $LiFePO_4$/CB/PHTPA/PVDF (8:32:50:10 wt%) composite cathode, which showed the ability to operate at high charge–discharge rates (20–100C) [110].

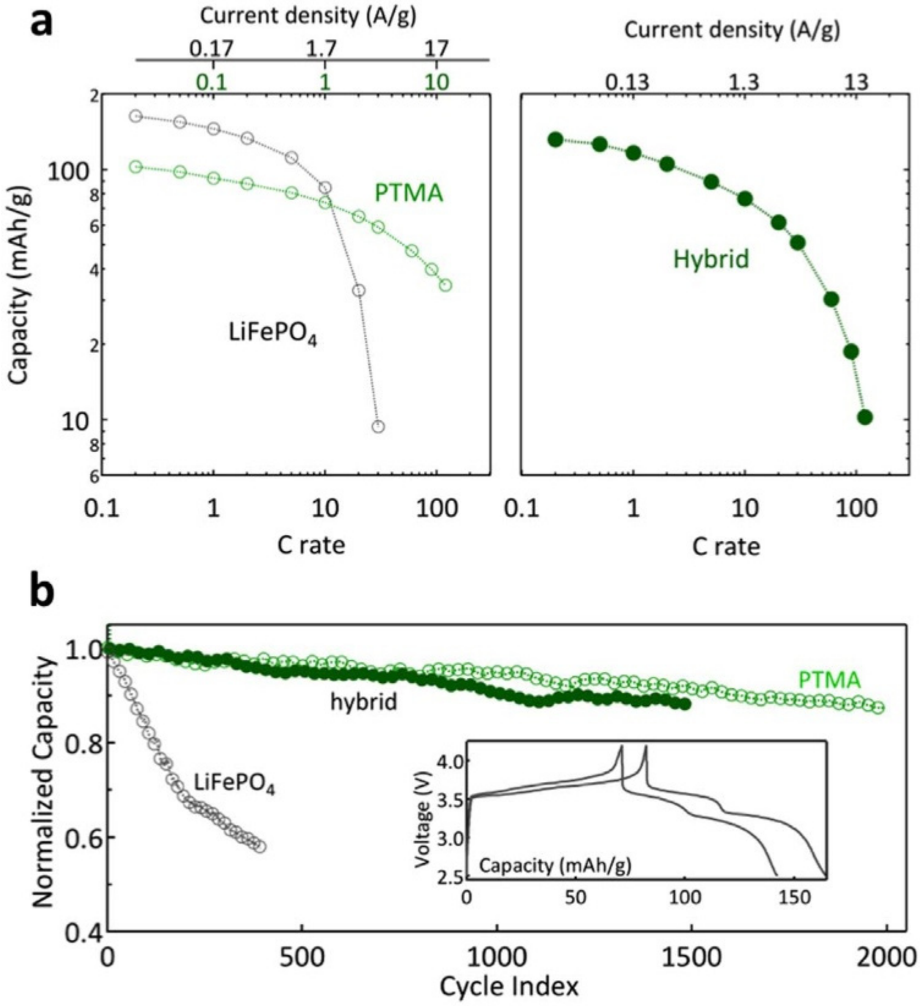

Figure 10. Electrochemical properties of the hybrid electrode. (**a**), Capacity retention function of C-rate and applied current density (symmetrical charge–discharge conditions) for $LiFePO_4$, PTMA and hybrid electrode. The green and black top axes correspond to PTMA and $LiFePO_4$, respectively. The rate of 1C corresponds to 100, 170 and 130 mAh/g for PTMA, $LiFePO_4$ and hybrid electrode, respectively. (**b**), Capacity retention at a charge–discharge rate of 5C for $LiFePO_4$, PTMA and hybrid electrodes. Inset: voltage profiles for the hybrid electrode at 1st and 1000th cycle [107]. Reprint with permission from [107]; Copyright 2014, The Author(s).

In contrast to the above described methods for the manufacturing of $LiFePO_4$/CA/EAECP/B composite cathodes implying the use of ex situ synthesized polymer as a slurry component, Cíntora-Juárez et al. developed an electrochemical in battery polymerization approach and proved its viability by preparing $LiFePO_4$-based electrodes containing PEDOT or PProDOT [111]. First, conventional cathodes were prepared by casting the slurry containing 85 wt% $LiFePO_4$, 8 wt% carbon black and 7 wt% PVDF onto aluminum discs, followed by drying. Then, according to the one-step method, the cathode was covered by a 0.02 M monomer solution in the battery electrolyte (the amount of the added monomer was 3.6 wt% of the total electrode mass), and used for assembling a cell. According to the two-step method, the cell with a conventional cathode was first charged at C/10 in order to perform the cathode delithiation and then opened inside the glove box to cover the cathode by the monomer solution. At the last step in both methods, the cell was galvanostatically charged at C/10, which caused the oxidative polymerization of EDOT and ProDOT monomers directly over the $LiFePO_4$-based cathode. All composite cathodes showed improved specific capacity (calculated based on the $LiFePO_4$ mass), enhanced rate capability and cycling stability as compared to the conventional sample (Figure 11) due to the good mechanical and electronic communication between $LiFePO_4$ particles facilitated by the conductive polymer grown in close contact with the active material. The best electrochemical results were obtained for the PEDOT-containing sample prepared by the two-step method, which was attributed to its higher conductivity of PEDOT versus ProDOT and indicated the advantage of the two-step cathode preparation procedure in the case of PEDOT. Electrodeposition of PEDOT over the pre-formed LFP and C-LFP-based conventional cathodes performed in a separate electrochemical cell before assembling a battery also yielded electrochemical performance improvement of the obtained composite cathodes over the baseline [73].

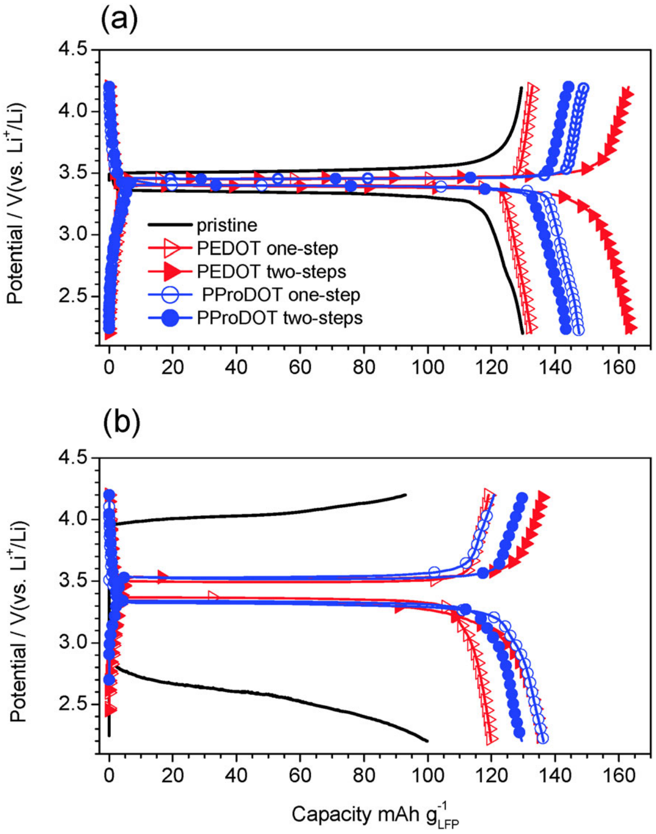

Figure 11. Charge–discharge plots for the different composites at (**a**) C/10 rate and (**b**) C rate [111]. Reprint with permission from [111]; Copyright 2014, Royal Society of Chemistry.

The use of both a conductive additive and a binder in combination with EAECP is a compromise solution that allows to compensate for the performance drawbacks of the conducting polymers when they are integrated into the lithium iron phosphate cathode structure. Unfortunately, the electrochemically inactive CA + B combination adds to the "dead weight" in the active layer, which limits the achievable gain in the electrode capacity.

Table 3. Synthetic strategies and electrochemical performance of lithium iron phosphate electrodes containing EAECPs as conductive binders.

Electrode Composition	**Synthesis Route**	**Initial Discharge Capacity, mAh/g (Per Active Materials)**		**Capacity Retention, %/Number of Cycles (Discharge Current)**	**Reference**
		At Low Discharge Current (Discharge Current)	**At High Discharge Current (Discharge Current)**		
		$LiFePO_4$/EAECP Cathodes			
C-LFP/PEDOT:PSS (92:8 wt%)	Casting a slurry of $LiFePO_4$ particles and a pre-synthesized polymer onto a current collector	120 (C/5)	-	close to 100%/100 cycles (1C)	[76]
C-LFP/PEDOT:PSS (91:9 wt%)		132 (C/10)	ca. 85 (1C)	close to 100%/50 cycles (C/2)	[80]
C-LFP/PEDOT:PSS (99.5:0.5 wt%)		147 (C/5)	122 (5C)	98%/100 cycles (1C)	[74]
LFP/SA-PProDOT (80:20 wt%)		137.6 (C/10)	100 (2C)	86.6% /400 cycles (1C)	[75]
C-LFP/C-PPy (85:15 wt%)	Casting a slurry of $LiFePO_4$ particles and a monomer onto a current collector followed by in situ chemical polymerization	150 (C/2)	60 (30C)	75%/500 cycles (1C)	[83]
C-LFP/PPy (80:20 wt%)	Electrochemical co-deposition of $LiFePO_4$ particles and a polymer matrix onto a current collector from $LiFePO_4$/monomer solution	154 (C/10)	ca. 110 (1C)	close to 100%/100 cycles (1C)	[86]
C-LFP/PEDOT (33.5:66.5 wt%), free-standing	Dynamic three phase interline electropolymerization (D3PIE)	75 (C/10)	52 (1C)	close to 100%/50 cycles (C/2)	[89]

Table 3. *Cont.*

Electrode Composition	Synthesis Route	Initial Discharge Capacity, mAh/g (Per Active Materials)		Capacity Retention, %/Number of Cycles (Discharge Current)	Reference
		At Low Discharge Current (Discharge Current)	At High Discharge Current (Discharge Current)		
LiFePO$_4$/CA/EAECP cathodes					
C-LFP/ CB/PANI (85:9:6 wt%)	Casting a slurry of LiFePO$_4$ particles, a conductive additive, and a pre-synthesized polymer onto a current collector	-	132 (1C) 116 (5C)	close to 100%/100 cycles (1C)	[90]
C-LFP/ CB/PEDOT:PSS (92:4:4 wt%)		165 (C/5)	155 (1C)	99+%/150 cycles (1C)	[92]
C-LFP/ CB/PEDOT:PSS (82:9:9 wt%)		148 (C/10)	ca. 100 (5C) 19 (20C)	74%/500 cycles (5C)	[94]
C-LFP/ MWCNT/PEDOT:PSS (82:9:9 wt%)		160 (C/10)	ca. 115 (5C) 56 (20C)	84%/500 cycles (5C)	[94]
C-LFP/ SWCNT/PEDOT:PSS (82:9:9 wt%)		166.6 (C/10)	ca. 120 (5C)	ca. 100 %/100 cycles (5C) 87.9%/2500 cycles (10C)	[80]
LiFePO$_4$/EAECP/B cathodes					
C-LFP/ PEDOT:PSS/CMC (96:2:2 wt%)	Casting a slurry of LiFePO$_4$ particles, a binder, and a pre-synthesized polymer onto a current collector	148 (C/5)	126 (5C)	99+%/100 cycles (1C)	[100]
C-LFP/ PEDOT:PSS/PEO (95:3:2 wt%)		143 (C/10)	ca. 57 (10C)	close to 100%/27 cycles (C/3) in sulfolane	[101]
C-LFP/ PEDOT:PSS/SPPO (95:2.5:2.5 wt%)		146 (C/10)	ca. 85 (10C)	99.4%/30 cycles (C/3)	[101]
C-LFP/poly-[Ni(CH$_3$-salen)]/PVDF (93:5.5:1.5 wt%)	Casting a slurry of LiFePO$_4$ particles, a binder, and a monomer onto a current collector, followed by in-battery electrochemical polymerization	142 (C/10)	ca. 84 (5C)	96%/150 cycles (C/2)	[99]
LiFePO$_4$/CA/EAECP/B cathodes					
C-LFP/CB/ PEDOT:PSS/CMC (92:4:2:2 wt%)	Casting a slurry of LiFePO$_4$ particles, a conductive additive, a binder, and a pre-synthesized polymer onto a current collector	148 (C/5)	128 (5C)	99+%/100 cycles (1C)	[93]
LiFePO$_4$/CB/ PEDOT:PSS/PVDF (84:8:1:7 wt%)		128.5 (C/10)	ca. 111 (2C)	close to 100%/50 cycles (2C)	[102]
C-LFP/CB/FP/PVDF (89.9:2:0.1:8 wt%)		135 (C/2)	59 (30C)	78%/2000 cycles (5C)	[106]

Table 3. *Cont.*

Electrode Composition	Synthesis Route	Initial Discharge Capacity, mAh/g (Per Active Materials)		Capacity Retention, %/Number of Cycles (Discharge Current)	Reference
		At Low Discharge Current (Discharge Current)	At High Discharge Current (Discharge Current)		
$LiFePO_4$/EAECP/B cathodes					
C-LFP/CB/PEDOT/PVDF (82:7.7:3.6:6.7 wt%)	In-battery electrochemical polymerization of the monomer cast over a pre-formed and delithiated $LiFePO_4$/CA/B electrode	ca. 135 (C/10)	ca. 107 (2C)	96+%/50 cycles (C/2)	[111]

3.3. EAECPs as Current Collector Coatings

Coating aluminum foil current collectors with carbon is a commercial technology, which prevents Al corrosion, facilitates the adhesion and reduces the contact resistance at the active layer/current collector interface thus improving the rate performance of $LifePO_4$ cathodes. Although carbon possesses many advantageous properties as pertains to its application as a coating material (high electrical conductivity, excellent mechanical and chemical stability, and corrosion resistance), it is yet another "dead weight and volume" material in the cathode structure [112].

Several studies suggested that EAECPs could offer advantages over carbon when used for coating the surface of the aluminum current collector [102,113–116]. Coating techniques based on oxidative chemical polymerization [102,113] and electrodeposition [114–116] have been proposed.

Lepage et al. produced a PEDOT coating on an aluminum foil in a multi-step process, which involved spraying the Fe (III) p-toluenesulfonate hexahydrate oxidant on Al, followed by introduction of EDOT by chemical vapor deposition (Figure 12) [113]. The thickness of such obtained PEDOT layer was comparable to the thickness of the current collector carbon coatings added to the Al surface in commercial products. The PEDOT-Al foil was coated with a C-LFP/CB/PVDF (85:10:5 wt%) active layer, and the performance of the resulting cathode was compared to the electrode with the same composition of the active layer coated onto a bare Al foil. The surface modification with PEDOT led to an improvement in the contact resistance between the current collector and the cathode active layer, which translated into a ~30% increase in the discharge capacity at 15C. Another study reported the use of a commercial PEDOT:PSS aqueous dispersion to produce a polymer coating over the aluminum current collector [102]. The authors found that PEDOT:PSS film between Al and $LiFePO_4$-based active layer tended to increase the electrode impedance but this drawback was compensated by an increase in the effective contact points between the current collector and the active material as the PEDOT:PSS coating adapted to the shape of $LiFePO_4$ particles. This resulted in a higher active material utilization and thus a substantial increase in the discharge capacity over the standard sample with a bare Al current collector. A significant improvement in the electrochemical performance over a conventional $LiFePO_4$ electrode (an increase in the discharge capacity by up to nearly 30% at 5C rate) was also observed by Ding et al. for a $LiFePO_4$/CB/PVDF (80:10:10 wt%) electrode assembled on the Al current collector modified by a sodium dodecyl sulfate (SDS)-doped PANI film [114]. The polymer coated onto the surface of the commercial Al foil using a cyclic voltammetry method had a leaf stalk-shaped morphology, which generated a relief-shaped surface and a transition conductive interface between two inorganic phases (Al and $LiFePO_4$). All these studies [102,113,114] demonstrated advantages of EAECP-coated Al current collectors over bare Al ones in terms of a promotional effect towards the electrochemical performance of $LiFePO_4$-based active layers. However, it remained unclear if the employed polymers provided any performance advantages over the carbon coating used in commercial C-Al foils.

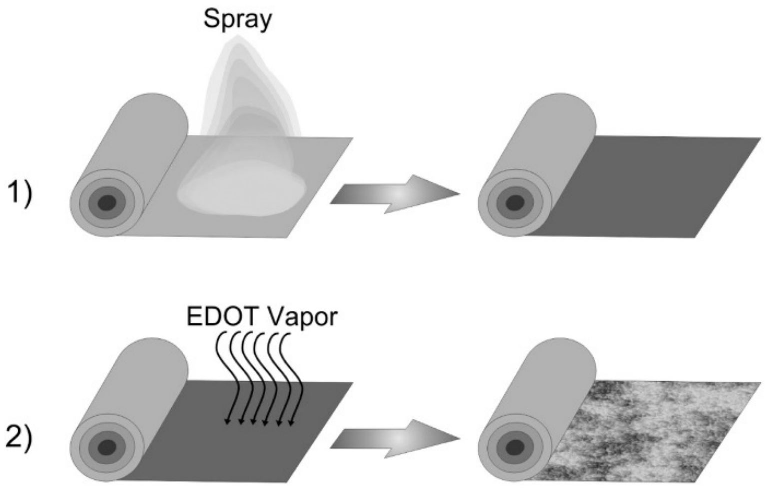

Figure 12. Schematic representation of PEDOT coating onto an Al current collector. (**1**) Aerosol deposition of Fe (III) p-toluenesulfonate hexahydrate. (**2**) Chemical vapor polymerization of PEDOT [113]. Reprint with permission from [113]; Copyright 2019, Elsevier.

The unconventional role of the EAECP as a current collector coating has recently been unveiled by Beletskii et al. who recently reported the use of a switchable resistance conducting layers of polymeric nickel complexes with the salen type ligands electrodeposited between the $LiFePO_4$-based active layer and the current collector (Figure 13) for overcharge protection of lithium-ion batteries [115,116]. The polymer layer showed sufficiently high electrical conductivity to support the cell operation within normal voltage range (Figure 13a) but acted as a reversible circuit breaker by sharply increasing its resistance upon overcharge up to 5 V (Figure 13b). At higher overcharge voltages, the overoxidized polymer turned into an insulating state and performed as an irreversible (single-use) circuit breaker [116]. This study offers a good example of adding functionality to the existing electrode component by capitalizing on the inherent characteristics of its material, which could be considered a promising direction for further research and development in the area of lithium ion phosphate batteries and other types of advanced energy storage devices.

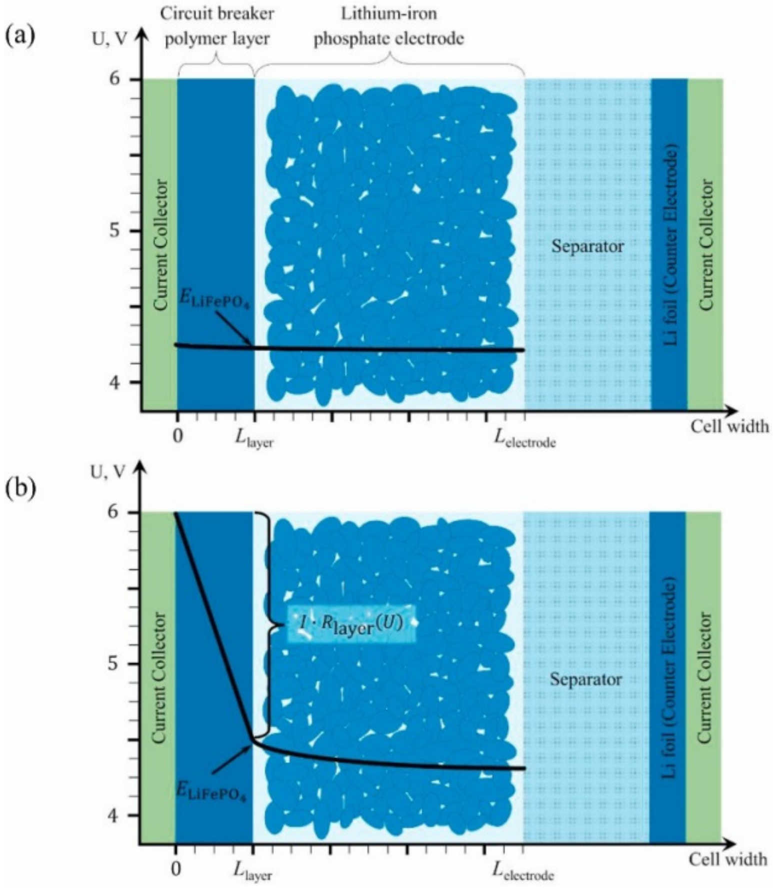

Figure 13. Schematic representation of the half-cell configuration with protective layer in (**a**) normal operation conditions and (**b**) at overcharge [116]. Reprint with permission from [116].; Copyright 2021, Elsevier.

4. Conclusions and Outlook

In this review, we presented a comprehensive overview of the electrode components based on electrochemically active electron conducting polymers for lithium iron phosphate LIB cathodes, main materials and methods for the preparation of EAECP components and their integration into the cathode structure. The studies discussed herein proposed replacing conventional carbon coatings, conductive additives, binders, current collector coatings, and sometimes even current collectors (for self-supported active layers) with EAECP-based formulations, with the aim of solving main drawbacks of $LiFePO_4$ (relatively low specific capacity, poor electronic and ionic transport) as compared to other advanced LIB cathode chemistries. As follows from the above discussion, almost every single one of the proposed approaches yielded a substantial enhancement in the electrochemical performance of EAECP-based $LiFePO_4$ electrodes, without any pronounced detrimental effects on mechanical properties or stability. Some of the cathode designs afforded significantly higher specific capacities through an increase in the active material loading and/or utilization and a non-negligible contribution of the polymer redox that turned "dead weight and volume" into an active space that stores electric charge. Other solutions minimized iron dissolution from the active material or enabled much desired fast charging options. Yet, none of the proposed $LiFePO_4$ cathode designs containing EAECP-based components has yet been adopted by the industry. At the root of this paradox lies an enormous gap between what academic research offers and what industry really needs.

In order for any technology to enter an advanced development phase on the path to commercialization, a clear understanding of its technical merits is required. In the LIB industry, it usually implies that technology performance should be demonstrated for electrodes with relevant active material loadings, thicknesses, densities and assessed by comparing with relevant baselines. Unfortunately, the composition and quality of research electrodes are usually far from industrial standards, so the overwhelming majority of potentially promising approaches never rise above the level of proof-of-concept studies.

At laboratory bench level, the lack of standardization in the LIB cathode preparation procedures make it close to impossible to compare compositions, designs, and methods developed by different research groups. Tiny details in the synthetic procedures and electrode processing protocols (reaction temperature, slurry mixing speed, drying speed, to name a few) have a potential to influence the cathode structure and performance parameters to the extent that it will overpower the effect of varying the chemistry of electrode components. In this respect, the specific capacity at various charge–discharge rates, cycling stability, mechanical strength, and other performance parameters reported in each particular study should be analyzed with caution to avoid misleading conclusions. That is why, in this review, we have opted to simply present a landscape of proposed electrode designs rather than to conduct a thorough head-to-head comparison in a search for a winning technology.

A close look at the methods for integrating EAECP components into the LFP cathode reveals numerous trades-offs between achieved performance and technical complexity of the proposed approaches. For example, two-component self-standing $LiFePO_4$/EAECP layers can potentially provide the most significant performance enhancement among other proposed composite electrodes but require the use of a polymer possessing a unique combination of functional properties. On one hand, subjecting lithium iron phosphate to strong oxidants or any other additional reagents as part of introducing EAECP components into the cathode structure may negatively affect the battery performance, especially in the long run, as trace amounts of chemicals can remain the electrode and unpredictably interact with cell parts during battery storage and functioning. From this perspective, using pre-synthesized polymer compositions appears more attractive than conducting chemical polymerization in situ. On the other hand, in situ methods provide more uniform and homogeneous polymer coatings over and between LFP particles than ex situ approaches. Electrochemical polymerization generates continuous three-dimensional highly conjugated web-like conductive structures that are usually unattainable by the chemical polymerization methods. At the same time, electrodeposition suffers from scalability challenges that chemical techniques face less frequently. From the material stand-point, the use of predoped EAECPs such as PEDOT:PSS enables constantly high conductivity of the composite over a wide voltage range but offer no gain in the specific capacity due to the polymer redox. On the contrary, the conductivity of pristine EAECPs depends on their doping level and may exhibit a bell-shape due to the limited conjugation, especially in the case of chemically synthesized materials, but such polymers will reversibly store additional charge.

With the low amounts of EAECPs that are used in the composite cathodes, the contribution of their electrochemical capacity to the overall capacity enhancement is often overseen and neglected, even if clearly present in the charge and discharge curves. However, it is not negligible. If we consider an active layer of a conventional $LiFePO_4$/CA/B cathode, which contains 90 wt% active materials and 10 wt% inactive additives, it will discharge 153 mAh/g (calculated based on the total mass of the active layer), assuming that the active material discharges its theoretical capacity (170 mAh/g). If we now substitute all inactive materials with EAECP that has redox capacity of 100 mAh/g, that will add 10 mAh/g to the active layer capacity, so that our hypothetical $LiFePO_4$/EAECP (90:10 wt%) electrode will discharge 163 mAh/g (based on the active layer mass), thus showing a 6.5% increase in the specific capacity over a conventional $LiFePO_4$/CA/B electrode. In reality, this number can be even higher because the theoretical discharge capacity of lithium iron phosphate is rarely attained in conventional electrodes, and the redox capacity of EAECP higher than 100 mAh/g is feasible. LFP battery manufacturers believe that such improvement in the active layer capacity can translate into non-negligible practically relevant battery capacity enhancement. Given that the industry exhausted most performance enhancement options related to the active material, the capacity improvement via replacing "dead weight" materials with EAECPs can make a big difference in the case of LFP-based electrode. In combination with other performance advantages offered by EAECP components, it can additionally strengthen the position of lithium iron phosphate as the LIB cathode material of choice.

As of today, none of the technologies reviewed herein appear to be ready for fast integration into the existing industrial cathode manufacturing lines. Current and near-future research efforts should be focused on developing cost-effective, easy-to-process formulations that can be efficiently scaled up for mass-production. Mechanical and electrochemical stability of the EAECPs should also be improved to make them applicable on the commercial scale. Most importantly, the current concept of testing arbitrary polymer formulations for battery applications should be replaced with targeted synthesis of EAECP materials with fine-tuned properties. That should make EAECP components fully competitive with more conventional approaches such as active material nanosizing and inorganic (carbon) coatings. With a high interest in electrochemically active electron-conducting polymers and their composites and perspective vigorous research developments backed by the industry demand, more intensive utilization of properties/functionalities of these polymer materials is expected to find its way into the field of advanced electrochemical energy storage.

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