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Intrinsically Conducting Polymer Binders for Battery Electrodes

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Definition: Binder materials are needed to keep particles of active masses in electrodes for batteries and supercapacitors together and to ensure their adherence to the current collector. Mostly synthetic polymeric materials are used. Because they are electrochemically inert, they do not add to the storage capacity of the electrode. Intrinsically conducting polymers ICPs such as polyaniline, polythiophene or polypyrrole can provide these functions also. They show electronic conduction because of mobile charge carriers generated in them by oxidation or reduction. In addition to providing the binder-function, they improve electronic conductance of the electrode mass because of their inherent conductivity and can also contribute to the charge storage capability of the electrode in the range of potential of the redox activity of ICPs in the used electrolyte solution. In most reports on the application of ICPs as component of conductive binders, their incorporation results in enhanced specific capacity and notable improvement of C-rate capability of electrodes. In addition, ICP binders provide partial or complete wrapping of grains of active electrode materials, which effectively inhibits the interaction with the electrolyte, suppressing side reactions and degradation of functional properties.

Keywords: batteries; supercapacitors; binder; intrinsically conducting polymers; polyaniline; polypyrrole; polythiophene

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1. Introduction

Intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity without added conducting materials. The commonly used ICPs can be classified into polypyrroles, polyanilines and polythiophenes. They have been of great interest to scientists since the initial discovery of ICPs with metal-type conductivities; they are still one of the most active areas of research in polymer science and engineering.

The conductivity in organic conducting polymers originates from alternating single and double carbon–carbon bonds in polymer chains, providing for π-orbital overlap along the molecular chain. As charge carriers in intrinsically conducting polymers electrons or holes may act, accordingly different states of ICPs are considered: *p*-doped state (achieved by oxidation of polymer segments, when an electron is removed from the valence band, leaving a hole, i.e., forming a positive charge) and so-called *n*-doped state (achieved by reduction of polymer segments, when an electron is added to the conduction band, forming a negative extra charge). Both doped states can be achieved electrochemically by oxidation or reduction of polymers. The created positive or negative charges during doping process are compensated by insertion of corresponding counter ions from the electrolyte solution.

Conducting polymers are attractive materials for use in a variety of applications because they combine the properties of electronically conductive and mechanically flexible materials. In particular, they have been proposed for numerous applications in metal-ion batteries as active electrode materials, for surface modification of active grains with thin coatings of ICPs, as conductive binder component in combination with various inorganic compounds in the cathodes and anodes of metal-ion batteries [1–4], early reviews focused on the binder-function in lithium-ion batteries are available [5,6].

Initially ICPs were proposed as single active material of battery electrodes due to their dopability and exchange of anions. A conducting polymer battery, for instance, such as a polypyrrole-lithium cell, operates by the oxidation and reduction of the polymer backbone. The positive charges created during charging are balanced by injection of electrolyte dopant anions, during discharge these are released back into the electrolyte solution. Simultaneously, lithium ions of the electrolyte are electrodeposited onto the lithium surface during charging and stripped during discharge. This charge–discharge process can be repeated about as often as in a typical secondary cell. However, the performance of such electrodes based on ICPs alone is not competitive due to their low specific capacity. The experimental values of specific capacities vary in the range 80–140 $\text{mAh}\cdot\text{g}^{-1}$ for commonly used ICPs, they also have the disadvantage of insufficient stability.

In addition, ICPs can act as electron-ion conductive matrices to ensure high electrical conductivity of composite materials and as binder component, providing mechanical integrity of electrode materials. In composites with different inorganic redox compounds used as battery electrodes (usually low conductive transition metal oxides, hexacyanometallates and others) they highly improve electrochemical performance for metal intercalation systems, as has been confirmed in many reports. These considerations and studies have been reviewed [5–7]. Despite of relatively low conductivity of ICPs in comparison with carbon additives their use in a composite is feasible due to their mechanical flexibility and their capability to buffer the volume changes during intercalation processes of inorganic solid components. This function of polymer binder also supports more reliable electrical contacts between inorganic active species and carbon species, reducing the interfacial Ohmic resistance.

However, it should be noted that the selection of specific ICPs as component of an electrode material is limited by their conductivity and stability within the specific electrode potential window in a given electrolyte solution. In this sense, most stable properties are obtained for PEDOT and PPy as components of battery electrodes within a wide potential window for alkyl carbonate electrolytes (approx. 2.5–4.2 V vs. Li/Li^+).

2. Methods of Preparation of Composite Electrodes with ICPs

Combination of inorganic rechargeable materials with ICPs is a promising method to obtain electrode materials for energy storage systems with high specific capacities, stability and C-rate capability. Composites based on inorganic nanoparticle-conducting polymer turned out to be promising systems for energy storage applications, due to enhancement of charge storage capacities and C-rate capabilities as well as to other unusual combinations of properties derived from the different components. The flexibility and stability of composite electrodes arise from their polymer components and functionality. In general, chemical or electrochemical oxidation is used for conducting polymer synthesis, therefore, the ensuing polymers are obtained in *p*-doped state. Many different methods of preparation of composite electrodes with conducting polymers have been proposed.

Among them are the following:

2.1. Mechanical Mixing and Blending Methods

ICPs in combination with inorganic compounds have attracted great interest as promising matrices for the construction of metal-ion batteries. The composite electrode materials can be prepared by mechanical mixing and pressing of powders of solid electroactive component and ICPs (sometimes with further additional binder and carbons). ICPs in such materials behave as a conducting matrix and contribute to the overall capacity. This technique of electrode preparation is low cost and suitable for large scale applications, leading to simple control of fractions of components.

2.2. Conductive Binder Based on ICP Dispersions

The term "binder" designates a material (in almost all cases a polymer), that is added to an electrode composed of particles to maintain the electrode integrity and to make a continuous electronic network by binding the active material and conducting additives together. Binder acts as a glue holding active materials and conductive agents together and on the current collector [8]. Polymers used as binders may have different nature and they are non-conductive, ionically conductive (polyelectrolytes) and mixed electron-ion conductive polymers. The latter represent the class of intrinsically conducting polymers. They provide the electrode integrity and the electronic and ionic networks between the active material and conducting additives.

One of the important challenges of application of ICPs is their processability, because ICPs cannot be dissolved in most common organic solvents. The use of ICP dispersions is a very convenient approach to overcome this hurdle. Usually, dispersions of ICPs can be obtained by doping of ICPs with macromolecular polyanions such as poly(styrene sulfonate) (PSS) (Figure 1) and some others.

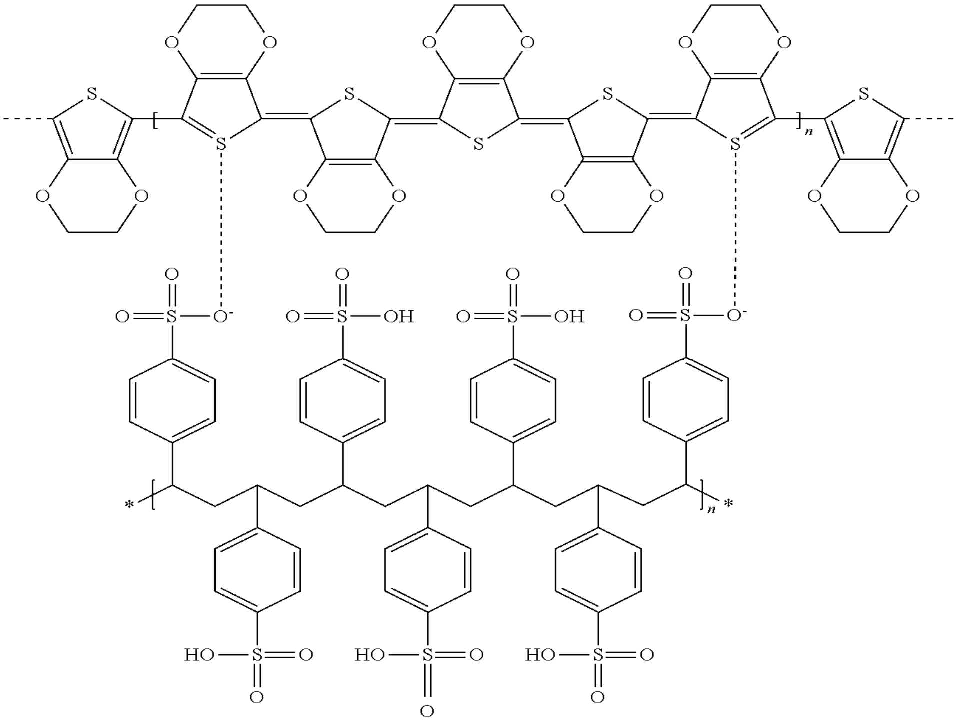

Figure 1. Structural scheme of PEDOT:PSS illustrating the interactions between ICP and counteranion (dopant anion) *: chain continuation.

Water-soluble dispersion forms of polypyrrole and polyaniline have also been synthesized by introducing alkyl side groups and combining with polyelectrolytes bearing hydrophilic side groups (–SO_3H, –COOH, –OH).

In this application ICP dispersions are playing a dual role as conductive and binding additive. However, the conductivity of ICPs is not always enough to provide electronic conductivity to the composites with active materials; therefore, the applied ICPs are combined with carbon additives and non-conductive polymers. Note that commonly used binders in battery electrodes such as polyvinylidene difluoride (PVDF) and polytetrafluoroethylene (PTFE) provide strong adhesion between other components, but they are electrical insulators. Consecutively, the use of these binders requires a significant fraction of conductive carbon additive. The use of ICPs reduces to a great extent the amount of carbon in electrode formulations.

In a number of studies dispersions of ICPs were used as an additional blending component to a standard-composition electrode containing a carbon additive and one of the conventional binders. In this case, on the one hand, there are positive effects of the introduction of the ICP, and on the other hand, there is almost no change in the process of preparation of the electrode, as well as good mechanical stability provided by traditional binders. As a further option, ICPs alone and in combination with other ion conducting polymers can act as the main binder, completely replacing traditional insulating binders.

Water-based binders with ICPs have received wide application in metal-ion batteries due to their environmental friendliness and safety issues. Different types of water soluble binders such as carboxymethyl cellulose (CMC), poly(acrylic acid), styrene butadiene rubber, sodium alginate and guar combined with ICPs were proposed improving the electrochemical performance of anode and cathode materials for lithium-ion batteries, zinc-ion batteries and others [9–23]. Especially wide application found the eco-friendly water-based binder poly-3,4-ethylenedioxythiopene with polystyrene sulfonate(PEDOT:PSS) dispersion combined with one of the aforementioned components. This combination showed positive effects on the functional properties of lithium ion batteries both in the case of negative electrode (Si, $Li_4Ti_5O_{12}$, etc.) [9–11] and positive electrodes ($LiFePO_4$, $LiFe_{0.4}Mn_{0.6}PO_4$, $LiCoO_2$ and $LiMn_2O_4$) [6,12–22].

Tuning the viscosity of the slurry of active electrode materials by use of large fraction of liquid conductive polymer dispersion is an option to support new techniques of electrode fabrication such as inkjet printing or spin-coating currently under development [24]. They also will enable more reproducible fabrication methods with control of micro-homogeneity of materials and their electrical conductivity.

2.3. Surface Modification of Active Materials

Many approaches have been proposed to improve the functional properties of energy storage materials by surface modification of active inorganic materials with various ICPs.

The main method of creating coatings from a conductive polymer is in situ oxidative polymerization on the surface of the particles of the active material starting from a monomer solution. This is a technically simple method that affords homogeneous films of ICPs under mild conditions. In situ polymerization prevents agglomeration of particles of inorganic material and contributes to their more uniform distribution. By variation of synthesis conditions films of different thicknesses and morphologies can be obtained, which makes it possible to create materials with specified properties.

Polypyrrol PPy is a very popular ICP for use in energy storage devices. It has a fairly high conductivity (several tens of $S \cdot cm^{-1}$), electrochemical activity in a wide range of electrode potentials (3.0–4.0 V vs. Li/Li^+) and a high theoretical redox storage capacity of 82 $mAh \cdot g^{-1}$ [25]. A common way to produce PPy thin films is in situ polymerization on particles of inorganic material. In this case, the inorganic material is mixed with a solution of monomer and dopant counter ion, forming a suspension, to which an oxidizing agent is further added. Various inorganic cathode materials have been studied: $LiCoO_2$ [21], $LiFePO_4$ [15,26–29], LiV_3O_8 [30,31], $LiMn_2O_4$ [32,33], $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$ [34], $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ [35], $LiNi_{0.5}Mn_{1.5}O_2$ [36], $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ [37] and $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ [38]. Most often, the reaction is carried out in water, the sodium salt of *p*-toluene sulfonic acid provides the dopant ion, and the oxidizing agent is $FeCl_3$.

Polythiophene Pty and its derivatives, with poly-3,4-eylenedioxythiophene (PEDOT) as the most interesting representative, have high electronic conductivity (up to 300 $S \cdot cm^{-1}$), good electrochemical and thermal stability, low redox potential and reversibility of charge transfer processes. Various inorganic materials were used in combination with PEDOT with in situ polymerization: $LiFePO_4$ [16,39,40], $LiMn_2O_4$ [41–43], TiO_2 [44], LiV_3O_8 [45], $Li_4Ti_5O_{12}$ [46–48] and $LiNi_{0.5}Mn_{1.5}O_4$ [20]. The material itself can act as an oxidizing agent. On its surface, oxidation of the monomer and precipitation of the polymer film will occur. For example, V_2O_5 and $LiFePO_4$ can oxidize EDOT molecules. The process is shown schematically in Figure 2.

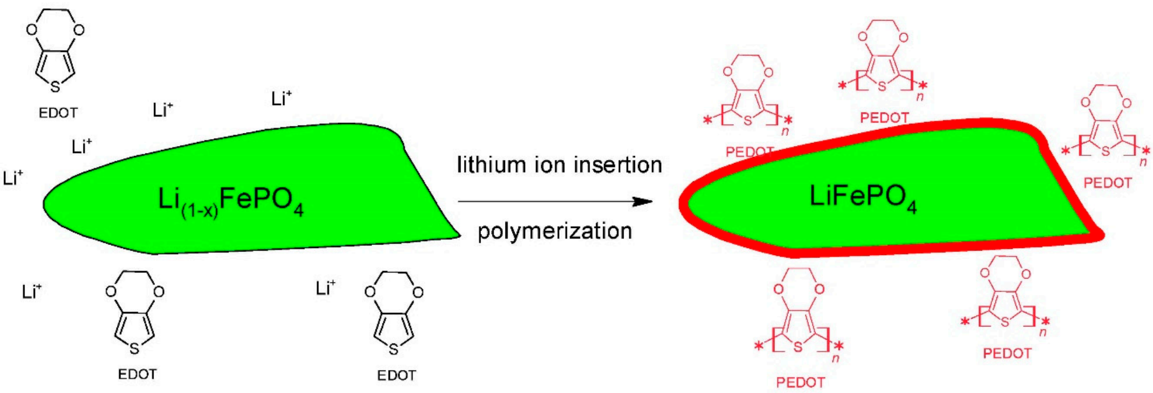

Figure 2. Scheme of coating of $LiFePO_4$ with PEDOT:PSS. *: chain continuation.

Polymerization can also be carried out directly on the surface of the material with a further oxidizing agent such as $FeCl_3$ or stronger oxidizing agents such as potassium permanganate $KMnO_4$ or ammonium persulfate $K_2S_2O_8$.

Another popular ICPs is polyaniline. The advantages of polyaniline include the simplicity and economy of methods for its production, high stability, good conductivity and electroactivity in a wide range of electrode potentials. A feature of PANI is the ability to change its physicochemical properties not only by changing the degree of oxidation and doping, but also by varying the acidity of the medium. The most common method of obtaining PANI is in situ oxidative polymerization enabling formation of thin and uniform films. Oxidative polymerization of polyaniline was used in the creation of coatings on a number of inorganic cathode and anode materials: $LiVPO_4F$ [49], $Li_4Ti_5O_{12}$ [50], $LiFePO_4$ [51–53], LiV_3O_8 [54–56], $Li_3V_2(PO_4)_3$ [57], $Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O_2$ [58] and others. As oxidizing agent ammonium persulfate is most often used in an aqueous solution of diluted hydrochloric acid.

Another common method of producing polymer coatings on particles of inorganic materials is deposition from polymer solutions or dispersions. This approach is easy to implement. In general, it is required to use an already pre-synthesized or commercially available polymer and dissolve or disperse it in a suitable solvent. After mixing with an inorganic material, the resulting suspension is stirred for some time, after which the resulting material is either filtered out or stirring continues when heated until the entire solvent has evaporated, thus leading to the deposition of the polymer directly onto the particles of the inorganic material. The amount of polymer incorporated in this approach is very easy to control by varying the concentration of the polymer solution or dispersion.

The application of ICP binder (ICPs dispersion or mixture with polyelectrolytes) mentioned above (Section 2.2) can be also considered as one way of surface modification by thorough mixing of active material powder with polymer dispersion.

A protective and conductive polymer shell can be formed on the surface of active grains by targeted oxidative chemical or electrochemical deposition from solution of the monomer.

As result, conductive binders facilitate the formation of electron and ion conduction pathways to enhance the metal ion transport to the interface and diffusion of ions into the bulk of electrode, providing an effective intercalation into solids. In the case of non-conductive binders (such as PVDF), this function is absent.

In most cases reported in the literature the formation of ICP layers on active grains of inorganic compounds resulted in improved electrochemical performance of electrodes (in terms of specific capacity, C-rate capability and stability during long-term cycling). In many studies, it has been shown that the coating with conductive polymers leads to an increase in Coulomb efficiency, especially for oxide cathode materials whose working potential range is above 4 V, for example, for $LiNi_{0.5}Mn_{1.5}O_4$ and $LiCo_xMn_yNi_zO_2$ [36–38,59,60].

However, the actually employed synthetic methods for surface modification are more complex and sophisticated than simple mechanical mixing or blending, so they may be less competitive for industrial scale application. Nevertheless, this provides a pathway to more reliable and uniform coatings of inorganic materials.

2.4. Chemical or Electrochemical Deposition on Electrodes

Composites of inorganic compounds with conducting polymers can be achieved by subsequent coating (or similar) of electrodes prepared with inorganic compounds by consecutive chemical or electrochemical deposition of conducting polymer layers. In particular, the template method can be applied by electrochemical synthesis of conducting polymers from monomer-containing electrolyte solutions into the pores of inorganic finely dispersed particles immobilized as a precipitate on the electrode. Monomers easily penetrate into pores of inorganic materials and form networks of polymers upon oxidative polymerization [61].

More sophisticated methods for the preparation of metal ion battery electrodes by chemical bonding of inorganic redox-active molecules to the backbone of a conducting polymers were also investigated.

2.5. Mechanisms of Electrochemical Performance Improvement of Electrode Materials by ICPs

Basically, many factors associated with the presence of ICP component in the electrode composition can affect the electrochemical performance. Some of them are specific, inherent in this electrode system and this polymer, and some of them are common to most electrode systems. Common effects of conductive binders, confirmed in the majority of investigations, are:

(i) The electronic and ionic conductivities of the composite electrodes are to a great extent enhanced by the use of conductive binders. The binders control the distribution of conductive additive and active material in the composite electrode and strongly influence the electron transport in the electrodes.
(ii) The use of small amounts of ICP dispersion leading to thin-layer coatings of active grains and short distances between them has been proven to be more effective for the improvement of the specific capacity and C-rate performance of electrodes.
(iii) The conducting polymers protect transition metal oxides from undesired redox reactions with the electrolyte components and from dissolution [62].
(iv) The polymer coating stabilizes the surface crystal structure and suppresses the phase transformation of the electrode material during charge–discharge cycles.
(v) The conductive polymer binder provides mechanical flexibility and can buffer volume changes during intercalation processes into inorganic solid components. It supports more reliable electrical contacts between inorganic active and carbon particles.
(vi) The conductive polymer improves the kinetics of interfacial charge transfer and bulk Li^+-ion transport, thus decreasing polarization.

Many examples demonstrating these functions and contributions of ICPs can be found in publications on the electrochemical behavior of their composites with inorganic electrode materials, for reviews see [25,63,64]. In most applications of ICPs as components of electrodes enhanced specific capacity of electrodes and higher C-rate capability result. In particular, the capacity of $LiFePO_4$/PEDOT electrodes was found to be 163–168 $mA \cdot g^{-1}$, close to the theoretical capacity of 170 $mAh \cdot g^{-1}$ for $LiFePO_4$ [5,6]. Effects of three different binders (PEDOT:PSS/CMC, CMC, PVDF) on oxide-based and phosphate-based positive and negative electrodes for lithium-ion batteries ($LiFePO_4$ (LFP), $LiFe_{0.4}Mn_{0.6}PO_4$ (LFMP), $LiMn_2O_4$ (LMO) and ($Li_4Ti_5O_{12}$ (LTO)) were examined [6,9]. The highest values of capacities at current density 0.2 C normalized to electrode mass ($Q_{electrode}$) were obtained for PEDOT:PSS/CMC-bound electrodes, they were on average higher than those for PVDF-bound electrodes by 12–15% for LFP, LFMP, LMO and LTO, respectively.

With the optimized formulation of electrode mass (Si/CMC/PEDOT:PSS/AB = 7:1:1:1 by weight), a silicon electrode exhibits the best electrochemical performance, retaining a specific discharge capacity of 1834 $mAh \cdot g^{-1}$ and a Coulombic efficiency of 98.5% after 100 cycles, with a small capacity fading rate of 0.4% per cycle [11]. The approach of replacing the traditional binder with PEDOT:PSS allowed us to increase the mass fraction of the active component ($LiCoO_2$) up to 99.5%, thus reaching extremely high capacity values of cathode of LIB 140 $mAh \cdot g^{-1}$ at a current of 0.2 C [17].

ICPs in composites also were demonstrated as effective components of cathodes in aqueous zinc-ion batteries. In particular, PANI-intercalated $V_2O_5 \cdot H_2O$ as cathode material demonstrated a high discharge capacity of 350 $mAh \cdot g^{-1}$ at 0.1 $A \cdot g^{-1}$ and outstanding cycling performance [25] better than in most previous studies. Similar improvement of V_2O_5 and VO_2 cathodes was achieved with PEDOT [23,65] with specific capacities of about 380–400 $mAh \cdot g^{-1}$ at 0.1 $A \cdot g^{-1}$. In all cases, the superior performance is largely attributable to the enhancement of the electronic conductivity and reinforcement of the layered structure with intercalated ICPs. This inhibits phase transformations and collapse of the layered structures.

The role of ICPs coatings is not limited to increasing the conductivity of the material, improving the electrical contact between the grains and with the current collector. The surface coating effectively changes the conditions for the formation solid electrolyte interfaces (SEI) at active grains, actually it can be considered as formation of artificial SEI layer, which has a significant role in enhancement of stability and cycling life of electrodes.

First of all, this is due to the blocking of the surface of the active material from direct contact with the components of the electrolyte solution. The decomposition of the components of the electrolyte solution on the surface of the cathode material leads to the formation of an SEI of complex composition. The composition of SEI can vary markedly depending on the electrode material and the used electrolyte, standard alkyl carbonate electrolyte solutions yield Li_2CO_3 and $ROCO_2Li$, which are formed during the reduction of alkyl carbonates, as well as LiF, which is formed during hydrolysis or dissociation of $LiPF_6$ [66]. Due to their low electronic conductivity, the components of the SEI covering the particles of the active material create additional resistance and voltage drop at the SEI boundary, which manifests itself in the form of an additional semicircle in the high frequency region in the EIS spectra in Nyquist plots. By blocking the surface, conductive polymers can significantly reduce direct contact with the electrolyte and inhibit the formation of SEI. This leads to a decrease in the resistance of SEI, both in the initial stage and after hundreds of charge–discharge cycles, which is confirmed by the data of EIS spectra. For examples of the development EIS spectra supporting this observation, see [20,58,67–69].

It should be noted that the change in the conditions for the formation of SEI is associated not only with mechanical blocking of the surface, but also with the possibility of interaction of heteroatoms of the conducting polymer or the conjugate system as a whole with surface atoms of the active material, which can also lead to inhibition of side reaction. This hypothesis was experimentally confirmed by an XPS study of $LiMn_2O_4$ coated with PEDOT [43]. New peaks corresponding to the bound manganese, sulfur and oxygen were discovered. Based on the analysis of the obtained results, the authors proposed a scheme for coordinating of the polymer to surface atoms.

The partial or complete coating of inorganic active grains can more effectively inhibit the interaction of the active material with the electrolyte and side reactions, reducing the degradation of electrode materials caused by dissolution and surface structural transformations.

3. Conclusions and Prospects

ICPs as components in composite electrodes for batteries and supercapacitors can replace the traditional binder materials; they may also even replace the carbon added for enhanced electronic conductivity of the electrode mass at least in part. Because the fraction of active material is relatively increased when the amount of added binder and conducting carbon is decreased, the specific storage capability of the electrode will grow. In addition, rate capability and stability are increased. These overall improvements suggest a closer look into more applications of ICPs in supercapacitor and secondary battery electrodes.

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