Intrinsically Conducting Polymer Binders for Battery Electrodes

Subjects: Engineering, Chemical

Contributor: Veniamin Kondratiev, Rudolf Holze

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

---

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][2][3][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 $mAh \cdot g^{-1}$ 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][6][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^+).

References

1. Holze, R. Composites and Copolymers Containing Redox-Active Molecules and Intrinsically Conducting Polymers as A ctive Masses for Supercapacitor Electrodes-An Introduction. Polymers 2020, 12, 1835.
2. Kondratiev, V.V.; Holze, R. Intrinsically conducting polymers and their combinations with redox-active molecules for rec hargeable battery electrodes: An update. Chem. Pap. 2021, 75, 4981–5007.
3. Holze, R.; Wu, Y.P. Intrinsically conducting polymers in electrochemical energy technology: Trends and progress. Electr ochim. Acta 2014, 122, 93–107.
4. Holze, R. Conjugated Molecules and Polymers in Secondary Batteries: A Perspective. Molecules 2022, 27, 546.
5. Nguyen, V.A.; Kuss, C. Review-Conducting Polymer-Based Binders for Lithium-Ion Batteries and Beyond. J. Electroche m. Soc. 2020, 167, 065501.
6. Eliseeva, S.N.; Kamenskii, M.A.; Tolstopyatova, E.G.; Kondratiev, V.V. Effect of combined conductive polymer binder on the electrochemical performance of electrode materials for lithium-ion batteries. Energies 2020, 13, 2163.
7. Fu, L.; Qu, Q.; Holze, R.; Kondratiev, V.V.; Wu, Y. Composites of metal oxides and intrinsically conducting polymers as supercapacitor electrode materials: The best of both worlds? J. Mater. Chem. A 2019, 7, 14937–14970.

Retrieved from https://encyclopedia.pub/entry/history/show/70286