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Applications of conducting polymers in energy

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Abstract

Conducting polymers (CPs), structures made on-demand, new composite mixtures, and possibility of deposit on a surface by chemical, physical, or electrochemical methodologies, have shown in the last years a renaissance and have been widely used in important fields of chemistry and materials science. This article will provide the basic definitions and fundamentals to understand state of the art of conducting polymers (CPs) in energy-related applications, particularly those related to electrochemical energy storage and photovoltaic conversion.

Keywords: Conducting polymers (CPs), energy storage devices, nanocomposites, polypyrrole (PPy) and polyaniline (PANi)

Introduction

Energy storage devices require electrode materials with good electronic conductivity to deliver maximum power. As a result, CPs are very attractive due to their broad range of conductivities, from that of semiconductors (10^{-11} to 10^{-3} S cm^{-1}) to that of metals (10^{-1} to 10^{6} S cm^{-1}) [1]. 3 Charge storage can be enhanced by controlling the synthetic parameters (i.e., doping agent, temperature, pH) or by designing different morphologies [2], with the aim of improving electronic conductivity, surface area, and redox activity.

Recent reviews [3] emphasize the development of CP-based materials for energy storage applications. The work of various authors [4-5] demonstrating the relationship between CP morphology and capacitance have led to the conclusion that the higher the aspect ratio of the CP nanostructure (they studied PANi nanospheres, nanorods, and nanofibers), the higher the specific capacitance. One example involves the hierarchically nanostructured conductive polymer gels, which have attracted attention in this field [6]. The enhancement is due to the increase in the level of oxidation/protonation of PANi, faster electrode kinetics, and higher surface area as the aspect ratio increases. PANi nanotubes showed a specific capacitance of 896 F/g at 10 A/g361 and cycling stability over 5000 cycles [4-5]. The dependence of CP pseudo capacitance on the size and packing of the CP nanoparticles has also been reviewed [7], leading to the conclusion that controlling the size and morphology of the CP does not improve its performance beyond an intrinsic limit. In general, conductive polymers are attractive in energy storage devices due to their high charge/ discharge cycling rate, high conductivity, large surface area, high specific capacitance, and good redox reversibility.

Conventional methods for preparing CP materials for electrode fabrication can be electrochemical or chemical in nature. Conducting polymers electrochemically synthesized directly on the current collectors as thin layers can have high electric conductivity and controlled doping level, as well as different morphologies [8-9]. Chemical routes, on the other hand, give polymers with low solubility and moderate conductivity [10].

Swelling and mechanical stress during cycling constitute the main problems of CPs in electrochemical energy storage. Usually, ions in the electrolyte must go in to and out of the bulk of the polymer many times to participate in faradaic and non-faradaic processes. As a consequence, intense research on electrode materials based on CPs bets on the synergetic effect of nanocomposites or hybrid materials, as well as on the use of large heteropolyanions as doping agents. For supercapacitors, electrodes based on graphene (GR)/CP nanocomposites are dominated by polypyrrole (PPy) and polyaniline (PANi) [11-12]. Graphene/polypyrrole (GR/PPy) composites have values near 300 F/g and good cyclability (i.e., 90% capacity retention after 500 charge-discharge cycles) [11], which are lower than the values obtained for nanocomposites based on (GR/PANi) [12].

Interestingly, the micromorphology of the PANi between the graphene layers was highly dependent on the dispersion medium [3]. Recent works related to PANi and PPy with carbon nanomaterials have addressed the interplay of heterogeneous electron transfer, electric double layers, and mechanical stability, as well as the importance of nanoscale blending and the use of free-standing membranes [13-14].

To obtain improved properties, a large number of recent works related to CP nanocomposites focused on CP and metal oxides [15], with most of the faradaic storage occurring in the oxide. In these composites, the CPs act as binding agents providing mechanical stability, porosity, and conductivity. ALD involves the conformal deposition of nanoscale thin films and surface layers down to atomic layers with high uniformity and well-controllable thickness and interface, leading to the enhancement of device performance [16]. ALD surface modification is most effective in battery-like electrodes, particularly LIB electrodes. As an example, an ALD RuO_2 layer on PANi nanowire surface, forming a PANi@RuO_2 core@ shell nanostructure, shows improvements in capacity, rate capability, and cycling stability [17].

Polyoxometalates are a large class of metal oxygen clusters of the early transition elements and some of the most promising building blocks for nanocomposites [18]. Regarding composites based on CPs and polyoxometalates (POMs), they are very promising in energy storage applications because the fast reversible redox reactions of POMs can be combined with the intrinsic redox activity of CPs [19]. Preparation of PANi−POM nanofibers shows remarkable improvements when compared to the bulk material, particularly on cycling stability.

CPs in Batteries

Taking into account that the desired characteristics in an electrode material are (1) electrochemical stability, (2) high specific capacity, and (3) a cost-effective preparation method, CPs are attractive because they are conductive, low cost, lightweight, and mechanically flexible. CPs improve the performance of electrode materials since they can accommodate large volume variations in large capacity oxides during the charge/discharge process. Several strategies to offset the low charge transfer kinetics of the redox process involve decreasing the oxide particle size, controlling its morphology, and introducing highly conductive materials such as CPs. Reducing the size reduces the diffusion path of charge compensated ions in the solid state, but it could also enhance spurious reactions with the electrolyte [20]. Liang *et al*. prepared a composite with SnO_2 loading on the surface of PANi−rGRO (reduced graphene oxide) by hydrothermal synthesis and used it as an anode for LIBs, obtaining 574 mAh/g after 50 cycles with a current density of 156 mA/g between 0.01 and 3 V [21].

CPs in Flexible Integrated Energy Systems

The performance of CPs in energy storage devices depends not only on their intrinsic properties but also on the microstructure and composition of the nanostructured or hybrid electrode.

A reasonable 2.1% overall energy conversion efficiency was obtained by integrating an energy wire with PANi/PANi and PANi/TiO_2 coated on a stainless steel wire as a supercapacitor and as a dye-sensitized solar cell, respectively [22]. More recently, a coaxial construction was reported with a polymer solar cell based on poly (3-hexylthiopene) (P3HT):[6,6]-phenyl-C60- butyric acid methyl ester (PCBM) fabricated on one part of a TiO_2 nanotube-modified Ti wire, and a supercapacitor made from CNT sheets attached on another part [23].

Conclusion

This article covers some of the recent advances of the use of conducting polymers nanostructures in energy applications. A good knowledge of the relationships among polymer components and their bulk properties will permit systematization of their construction. This would open the gate to a vast possibility of applications based on the individual properties of the components and of their mixtures to finetune desired properties. This would open the gate to a vast possibility of applications based on the individual properties of the components and of their mixtures to finetune desired properties.

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