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Intrinsically conducting polymers in electrochemical energy technology: Trends and progress

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ABSTRACT

The use of intrinsically conducting polymers (ICPs) like polythiophene (PTh), polypyrrole (PPy) and polyaniline (PANI) in devices and systems for electrochemical energy storage and conversion is briefly reviewed with a focus on an overview distinguishing between already established uses and potential applications. Basic principles in these three major fields are highlighted:

- ICPs as active masses.
- ICPs as conductance-enhancing additives.
- ICPs as auxiliary materials beyond conductance.

1. Introduction

Intrinsically conducting polymers, such as polyaniline and polypyrrole, have a long and a short history [1–3]. The long one presumably starts with a report by Runge [4], who observed a black product when treating aniline with oxidizing agents. These products were described in more detail later by Fritzsche [5]. Letheby [6] observed formation of a dark, electrochromic product after anodic oxidation of aniline. Goppelsroeder [7,8] identified this as aniline oligomers. The product, later called aniline black (nigraniline), hardly gained prominence beyond the frequently invoked use in black shoe-polish. All this changed with the observation of a huge increase in electric conductance upon oxidation of polyacetylene by addition of iodine studied and reported by Shirakawa et al. [9]. This is where the modern (and thus short) history of conducting polymers starts. The present knowledge of structure and properties helpful for the applications briefly reviewed here is the result of a long way starting with the first tentative descriptions by Goppelsroeder [7,8] and later by Green and Woodhead [10] and Willstätter and Dorogi [11].

The highly unusual combination of properties: Materials composed essentially of carbon, hydrogen, some sulfur, nitrogen or oxygen, i.e. typical constituents of organic molecules and polymers, showing metal-like electric properties has inspired researchers to propose numerous applications in almost all branches of science and technology [12]. Currently ICPs are widely used in electrolytic capacitors (Tantalum type [13]), beyond electrochemical energy technology their use in printed circuit board production when making through-contacts is well established. Reviews related to the subject contemplated here have been published including a report on recent advances of PANI composites with metals, metalloids and nonmetals only touching briefly on some general applications [14] and on metal nanoparticles embedded in ICPs [15].

2. The applications

Among the numerous initial suggestions were applications in electrochemical energy technology in secondary batteries and in fuel cells.

Some studies of catalytic effects of e.g. PANI-layers for electrode reactions not related to energy conversion (e.g. [16–18] or in sensors) are not treated here (for overviews see [19,20]). Studies of pyrolysed ICPs subsequently used as catalyst support are also not reviewed here (see e.g. [21]).

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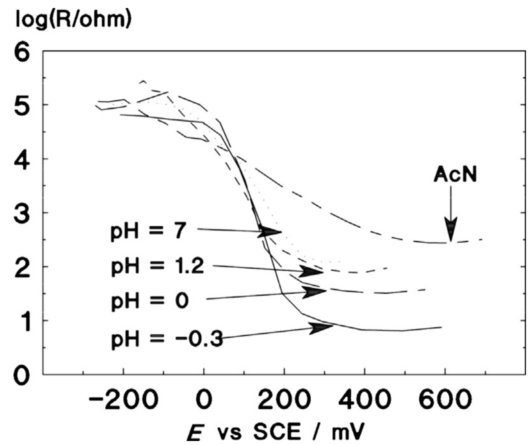

Fig. 1. Change of electronic resistance of PANI as a function of solution pH and electrode potential [1].

The name-giving property – the intrinsic electronic conductance[2] – showing large variations as a function of electrode potential and sometimes of other experimental or environmental variables (like pH in case of polyaniline) is illustrated in a typical example in Fig. 1. Because of the pronounced dependence of electronic conductance on state of oxidation (degree of doping etc.), i.e. the electrode potential, in any application the ICP must either be always kept at a sufficiently positive (or negative) electrode potential or otherwise conductive additives like graphite or graphene must be added. Otherwise only mechanical, non-conducting capabilities will be utilized. Because these various beneficial effects cannot always be separated clearly following the claims of the authors, their interpretation of results and most likely conclusions are summarized first with respect to fuel cell applications, then to batteries, and finally to supercaps. Because of this pronounced dependence of conductance not only on degree of oxidation of the ICP, but also on pH of solution and other factors the actual use has been further complicated.

2.1. ICPs in fuel cell applications

The application in fuel cell electrodes was considered as a promising remedy of the even today unsolved problems of chemical long-term stability of the catalyst support (if the electrode is not entirely composed of catalytically active material), reduction of sensitivity towards poisoning reaction intermediates, stable dispersion of catalyst material and mechanical–structural stability.

Applications can roughly be grouped into use of ICP as (1) a support (structured or simply unstructured – as obtained); (2) coating on a structured support of another material (e.g. PANI on carbon fibers); (3) part of a composite (e.g. PANI with platinum particles inside); and (4) coating on the catalyst (e.g. PEDOT on platinized carbon) (although the experimental descriptions are sometimes less than conclusive about the actual setup and structure). This organization is far from perfect, it may fail sometimes because of either misunderstood descriptions of procedures and/or results or because a given system may fall into more than one class (e.g. a composite coated additionally with an ICP).

Most frequently methanol oxidation was employed as a test reaction starting with the first report on PANI modified with electrodeposited platinum microparticles [22], presumably because of the interest in direct methanol fuel cells. Only infrequently ethanol oxidation was studied. Preferably acidic electrolyte solutions (or systems, like proton-conducting membranes) were used, in case of e.g. gold as catalyst also alkaline solutions were employed. A review of platinum-doped PANI and PPy as catalysts for electrooxidation of small organic molecules has been provided with particular attention to the frequently observed reduction in electrode poisoning [23]. An overview of metal-ICP nanocomposites with particular attention to analytical applications is available [24]. Activation energies for some electrooxidation reactions of molecules potentially of interest in sensors and fuel cells have been obtained for platinum-modified PPy and PANI [25]. Only infrequently PANI and other ICPs have been used in positive electrodes for e.g. dioxygen electroreduction.

2.1.1. ICP as a structured support

PPy electrodeposited on aluminum alloy 110 was used as catalst for methanol oxidation in an aqeous solution of 0.1 M $KClO_4$ [26]. Adsorbed species formed on the ICP-layer were apparently not inhibiting the catalytic activity. Nanofibrous PANI alone and coated with electrodeposited Pt–Ru as studied by Zhou et al. [27] showed a considerable electrocatalytic activity in particular with the metallic coating and good long-term stability. Platinum on nanofibres of PANI showed higher catalytic activity than platinized carbon [28]. PANI tubules were used as catalyst support for platinum with better results in methanol electrooxidation than with conventional platinum-loaded (20 wt.%) Vulcan XC-72 [29]. Platinum incorporated into poly(3-methyl)thiophene showed an effective platinum dispersion and high utilisation of the metal catalyst in methanol oxidation [30]. Kim et al. [31] compared the catalytic activity of hollow sphere PANI prepared via a silica particle-template based procedure with γ-irradiation and subsequently loaded with gold particles with that of simple PANI loaded with gold; a 1.3-fold increase of methanol oxidation current in alkaline solution was found. Also in alkaline solution electrodeposited nickel in PANI was identified as a catalyst for methanol electrooxidation [32]; similar results were obtained with copper instead of nickel [33]. Addition of platinum or palladium further enhanced the catalytic activity. Palladium–PANI nanofibres showed excellent electrocatalytic activity for oxidation of methanol, ethanol and formic acid in both acidic and alkaline electrolyte solutions [34]. Huang et al. compared the influence of PANI morphologies on catalyst performance after modification with platinum [35]. Best results were obtained with fibers. Network-structured PANI and PPy modified with platinum and silver were explored as electrocatalysts for methanol oxidation by Tang et al. [36]. Excellent activity was observed. Composites of PEDOT and mesoporous carbon were prepared by Tintula et al. [37] and subsequently modified with platinum. They showed superior stability when compared with XC-72, this was attributed to improved corrosion resistance of the carbon component. PEDOT doped with poly(styrene sulphonic acid) PSSA was proposed as alternative electrode support subsequently modified with platinum [38]. Reductions in the needed amount of Nafion and lower corrosion than found with XC-72 were observed.

2.1.2. Coating on a structured support

Surface-functionalized multi-walled carbon nanotubes (MWCNTs) are embedded in PANI by electropolymerization of aniline from a solution containing MWCNTs [39]. Finally platinum was electrodeposited onto this composite material. The addition of MWCNTs resulted in a superior performance of the material as an electrode for formic acid electrooxidation. The electrode potential was in a range where PANI is highly conductive. The role of PANI beyond being simply the support is not discussed. The significantly improved stability and the microscopy images showing platinum deposited mostly on the MWCNT embedded in PANI

[2] Frequently the term conductivity, i.e. specific conductance – is used. Because of most likely insurmountable experimental problems no specific reproducible values are available and will not become available. The present report thus sticks with conductance.