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Invited Lecture-3

Storing energy in Plastic: Intrinsically Conducting Polymers in Electrochemical Energy Technology



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The possible uses of intrinsically conducting polymers in systems for electrochemical energy conversion and storage are reviewed with an initial view at possible options and limitations, followed by a presentation of selected applications highlighting their particular function in a given application. Finally the current status is inspected, possible directions of further research and development are outlined.

Almost immediately after the discovery of the highly variable electronic conductivity of intrinsically conducting polymers IC like polyaniline PANI, polypyrrole PPy, polythiophene PTy and many more which could be prepared and modified electrochemically a flood of suggestions for applications followed [1,2].

Among these uses application in batteries and fuel cells featured prominently. Somewhat later – corresponding to the rising interest in supercapacitors – their use in these devices was proposed also. Given the merger between battery and supercapacitor materials [3-7] and the similar disappearance of boundaries between secondary and primary batteries this was to be expected. Reviews covering various parts of the field at different states of development are available [8-16].

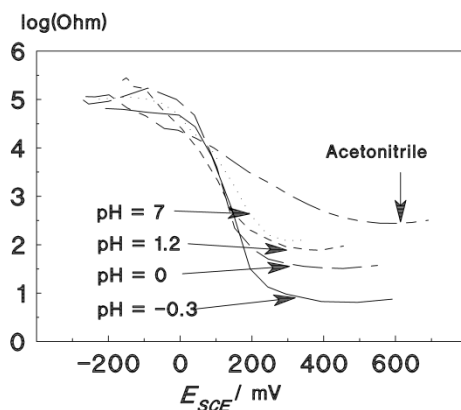
The function of ICPs in all devices can be:

- Active mass in batteries and supercapacitors or catalysts (in fuel cells)
- Support of active material (catalyst in fuel cells)
- Conductivity enhancer in active materials
- Protective coating of active materials

In some cases not the ICP itself but its pyrolysis products have been employed. Because the result of pyrolysis is basically a more or less degraded material containing carbon and – depending on the used ICP – nitrogen or sulfur these uses are not considered here [17].

ICPs in batteries

Initial optimism stimulating development of PANI and PPy into battery electrodes ended in rather early frustration, first products disappeared rapidly from the market [18]. In addition to conceivable compatibility problems (cell voltage incompatible with current usage) stability might have been an issue. Overwhelming stability of most ICPs is still frequently reported in research publications, but the duration of tests – if lifetime tests have been done at all – is almost everytime inadequate. A second issue overlooked almost everywhere is the dependence of the conductivity on the electrode potential i.e. the degree of oxidation. In case of PANI the influence of pH adds a further dimension to this problem:



Change of conductance of a polyaniline film as a function of electrode potential in different electrolyte solutions (for details see [19-20])

Instead of use as an active material ICPs have been proposed as additives to improve electronic conductance of poorly conducting active materials and to improve mechanical and/or chemical and thus in turn overall stability of materials showing fragmentation and pulverization as a consequence of shape change. Coating of LiV_3O_8 with polypyrrole made this composite suitable as negative electrode material for aqueous rechargeable lithium batteries by inhibiting release of vanadium ions into the electrolyte solution [21]. A composite of poly(3,4-ethylenedioxythiophene) and LiFePO_4 prepared by chemical reaction of 3,4-ethylenedioxythiophene with lithium-poor $\text{Li}_{1-x}\text{FePO}_4$ was identified as a promising positive electrode material for lithium ion batteries [22].

ICPs in fuel cells

Lack of catalytic activity and stability of properties has hampered use of ICPs in this application. For the dioxygen reduction reaction activity beyond that of plain carbon materials has rarely been observed, if any was observed at all no attempts were made to distinguish between simple surface effects (increased surface area because of porosity) and true catalytic activity. Oxidation of organic fuels has been studied with similar results. ICPs have been used as supports of common, mostly metallic, catalyst materials. Their use as protective layer on negative electrodes has turned out to be particularly effective *Error! Bookmark not defined.*

ICPs in supercapacitors

In the quest for higher gravimetric and volumetric energy densities of supercapacitors utilization of superficial redox processes (the term pseudocapacitive processes is frequently used incorrectly) are intensely studied because the currently employed carbon materials [23-37] will most likely not meet challenging development goals. At first glance the rather low gravimetric charge density (both theoretical and experimentally observed one [9]) of all ICPs when compared with data for many redox-active metal oxides looks unalluring. Nevertheless many studies of ICP-supercapacitor electrodes have been reported, even studies of complete supercapacitors of the symmetric design, i.e. an arrangement with two identical ICP-electrodes, despite the obviously very limited utilization of the active materials [13] and the presumably limited suitability of an ICP in its neutral and poorly conducting state as a negative electrode. Only in a few studies the electronic conductance of electrode materials has been addressed, reliable data are basically unknown. Many authors employ addition of carbon in various forms for improved conductance, in addition thin film setups tend to limit the detrimental effects of poor conductance. Unfortunately the amount of additions is purely



empirical, they drive down energy density because the additives do hardly contribute to storage capacity.

Numerous metal oxides have inherent drawbacks like poor electronic conductivity, mechanical deterioration because of volume change even during superficial redox reactions, alternatives to the standard addition of conductivity-enhancing carbon materials and various binders have been studied. ICPs have attracted considerable attention as possible replacements for both additives contributing in addition to charge storage capability. Numerous types of composites and preparation procedures have been reported [38]. The mode of operation, i.e. what is the ICP doing, is unclear in most reports, it certainly will depend on the way composites are prepared and on the morphology of the product. In some cases evidence suggests that a coating with an ICP hinders dissolution of the metal oxide and keeps the metal oxide in place even after volume changes. In case of nanoparticles embedded in a matrix of ICP the assumed electronic conductivity ameliorates problems caused by low conductance of the metal oxide, again volume change effects are compensated. An external coating of an ICP with metal oxide particles will hardly avoid dissolution and protection, it will only guarantee sufficient mechanical and electronic contact with the metal oxide. Studies which might shed some light onto the various functions and their specific contributions for a given case are lacking. Unfortunately reported stability data – if there are any reported at all – are not very promising. Given the respective data for electrochemical double layer capacitors (EDLCs) showing 100000 and much more cycles at stable performance composite electrodes rarely show constant behavior for more than a very few 10000 cycles.

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