POLYACETYLENE ELECTRODES FOR NON-AQUEOUS LITHIUM BATTERIES

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Summary

Polyacetylene can be electrochemically oxidized in a cell of the type $Li/LiClO_4$ in propylene carbonate/CH_x with nearly 100% coulombic efficiency for doping levels (y in $[CH(ClO_4^-)_y]_x$) of less than 0.10. At higher values, the electrochemical potential of the oxidized film is above 3.9 V *vs.* Li, and the electrolyte is unstable.

Reduced polyacetylene $(Li_yCH)_x$ can serve as a non-aqueous battery anode in the traditional role of lithium. However, stable voltages and high coulombic efficiencies in an electrolyte of 0.8M $LiClO_4$ in tetrahydrofuran are only observed at reduction levels of $y <$ about 0.10. In addition, the potential of a polyacetylene anode doped with Li^+ is 0.5 - 1.5 V positive to that of Li in the same solution. At present, polyacetylene electrodes are rather unstable, sensitive to impurities, and characterized by low volumetric energy density and low-to-moderate gravimetric energy density. They do not appear to offer major advantages for use in high energy density, rechargeable, non-aqueous electrochemical cells.

1. Introduction

Polyacetylene is a simple, conjugated organic polymer which can easily be prepared as a film by the catalytic polymerization of acetylene. When polyacetylene films are exposed to oxidants such as iodine and bromine, the films oxidize to form compounds of the type, $(CHX_y)_x$. Films can also be reduced to compounds of the type, $(M_yCH)_x$ in which M is typically Na and Li. The oxidation or reduction of polyacetylene transforms it from an electronic insulator to a lustrous polymer with an electronic conductivity typical of metals [1 - 3].

These oxidation and reduction reactions can also be carried out electrochemically in non-aqueous electrolytes containing appropriate dissolved anions and cations. The electrochemical potentials of the oxidized films are 3 - 4 V *vs.* a Li electrode. The potentials of the reduced films are about

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0.5 - 1.0 V positive of that of Li. Polyacetylene can therefore function as either an anode or a cathode in a non-aqueous battery.

The critical questions concerning the attractiveness of polyacetylene for actual electrochemical energy storage concern its volumetric and gravimetric capacity (value of y that can be attained), its voltage as a function of y, and its stability.

Our research has explored these aspects of the chemical and electrochemical reactions of polyacetylene. Much of this work on the stability [4], oxidation [5], and reduction [6] of polyacetylene has been reported elsewhere. This paper briefly reviews the preparation and properties of polyacetylene and summarizes our findings.

2. Physical and chemical characteristics of polyacetylene

The polymerization of acetylene into polyacetylene was first described by Natta *et al.* [7], who produced polyacetylene powder by bubbling acetylene gas through a solution of $TiCl_3$–$AlEt_3$ catalyst. The resulting polyacetylene was found to be a linear polymer predominantly in the *trans* form. The preparation of films of polyacetylene was first described by Shirakawa *et al.* [8]. Shirakawa reported that polyacetylene films can be synthesized by wetting the walls of a glass reactor with a toluene solution of $Al(C_2H_5)_3$–$Ti(n-C_4H_9)_4$ Ziegler catalyst and then admitting acetylene gas at pressures ranging from a few Torr to an atmosphere. A film of polyacetylene grows on the surface of the catalyst solution and on any surface that has been wetted by it.

Physical characteristics

The physical characteristics of polyacetylene films depend on the temperature, pressure, and time involved in their synthesis. Thicker films are produced at higher acetylene pressures and longer polymerization times. In general, polyacetylene films have a randomly-oriented fibrillar structure. The fibrils are typically 50 Å to 200 Å in diameter. Shirakawa's original work [8] found that film morphology varied slightly with temperature. Films prepared at −78 °C had fibril diameters of about 200 Å, while the average fibril diameter in films prepared at 100 °C was about 300 Å. The bulk density of typical polycrystalline polyacetylene is approximately 0.4 g/cm^3 [9]. Polymer fibrils fill only about one-third of the total geometric film volume. The actual surface area of the films is quite large, about 40 - 60 m^2/g.

Polyacetylene forms in either *cis* or *trans* isomers. The *cis/trans* ratio depends on the polymerization temperature. The *cis* isomer can be produced at −78 °C, but it is unstable toward isomerization, which can be induced by heating or by chemical doping [10].

The *cis* and *trans* isomers are quite different in their superficial physical properties. *Cis* films are flexible and can be easily stretched at room tem-

perature to about three times their original length [1]. *Trans* films are relatively brittle. Stretching *cis*-polyacetylene tends to orient the films along the lines of stretch [8].

Stability

Various authors have investigated the stability of polyacetylene [11 - 14]. Virgin, undoped *cis*-polyacetylene isomerizes spontaneously, as has just been described, and self-reacts forming cross-links and defects. These reactions occur rapidly at elevated temperatures (150 - 260 °C) [10].

Polyacetylene, when not in contact with an electrolyte, reacts rapidly with oxygen [4]. Oxidation takes two general forms. When exposed to small concentrations of oxygen at low pressures, it appears to be reversible, at least for short exposures. Under these conditions, oxygen reversibly reacts with the conjugated polymer chain in the prototypical reaction generally referred to as 'p-doping'. However, upon exposure to oxygen for longer periods of time, the reaction is irreversible, the polymer becomes brittle and even more insulating than either virgin *trans* or *cis* film. The latter reaction involves the irreversible oxidation of the polymer chain and degradation of the conjugated bond network.

We have carried out extensive thermogravimetric analysis, differential scanning calorimetry, and conductivity measurements to determine the stability of doped polyacetylene films. All of the results indicate that such films are unstable at moderate temperatures. Films doped with iodine or bromine decompose between 45 and 55 °C. Films which contain AsF_6^- as the guest ion are somewhat more stable. The decomposition reactions are irreversible. They decrease the electronic conductivity of the material and ultimately destroy its usefulness as an electrode.

3. Electrochemical investigations

Interest in the electrochemistry of polyacetylene began with the demonstration by Nigrey *et al.* [2] that polyacetylene can be electrochemically oxidized. They produced the first ClO_4^- doped polyacetylene by oxidizing a sample in a 0.5M solution of tetrabutylammonium perchlorate in methylene chloride at 9 V *vs.* a counter electrode. After one hour, the film had the composition, $[CH(ClO_4)_{0.0645}]_x$ [2]. They extended their investigations to show that the electrochemical oxidation of polyacetylene can be reversed and the oxidized material reduced to the original composition [15]. This reversibility is critical to the application of polyacetylene in batteries.

Subsequent work demonstrated that polyacetylene can be electrochemically reduced to the n-doped form. MacInnes *et al.* [3] showed that a polyacetylene electrode is spontaneously reduced when shorted against a lithium electrode in tetrahydrofuran containing $LiClO_4$. Similarly, polyacetylene can be reduced in a solution of tetrabutylammonium salts in

propylene carbonate or tetrahydrofuran to form n-doped compositions containing the tetrabutylammonium cation [3].

These initial experiments led to the suggestion that polyacetylene films might be used as polymeric ion insertion electrodes in batteries. MacInnes *et al.* [3] have described batteries using polyacetylene anodes, polyacetylene cathodes, and both anodes and cathodes of polyacetylene.

4. Summary of our research

Our research has examined the oxidation (p-doping) of polyacetylene in propylene carbonate containing $LiClO_4$ and $LiAsF_6$ and the reduction (n-doping) in tetrahydrofuran containing $LiClO_4$. Its principal goals have been to explore the reversibility, coulombic efficiency, and electrochemical potentials associated with the reactions at various levels of doping.

The polyacetylene films used in these experiments were kindly provided by Prof. A. MacDiarmid and co-workers from the Department of Chemistry of this University.

The electrochemical measurements were carried out in a small, three-compartment cell. The polyacetylene electrodes (approximately 1 cm^2 and 0.01 cm thick) were held in Pt mesh between the lithium reference and lithium counter electrodes. The capacity of the cell was about 1 cm^3.

Electrolytes were prepared from Burdick and Jackson solvents which were distilled and percolated through neutral activated alumina (Woelm). The electrolyte salts were $LiAsF_6$ (U.S. Steel, Electrochemical Grade), $LiClO_4$ (Alfa-Ventron), and $LiClO_4$ (Anderson Physics). The salts were dried at 180 °C before use. After the salts were dissolved, the electrolyte solutions were purified by a second percolation through activated alumina.

Electrochemical oxidation of polyacetylene
When a polyacetylene film is electrochemically oxidized in propylene carbonate with ClO_4^- or AsF_6^- as the anion, its open circuit potential varies from about 3.6 V (*vs.* Li/Li$^+$) at $y = 0.01$ to about 3.9 V at $y = 0.10$. Oxidation proceeds smoothly at 50 $\mu A/cm^2$. Subsequent reduction at 500 $\mu A/cm^2$ extracts about 40 - 60% of the stored charge before the potential reaches 2.5 V. Nearly all of the remaining charge can be recovered by an extended (10 - 20 h), controlled potential discharge at 2.5 V. Within this composition range of $0 < y < 0.10$, the oxidation/reduction coulombic efficiency (Q_{out}/Q_{in}) is 90 - 100%.

At least two factors strongly influence the coulombic efficiency of oxidation/reduction. If the liquid electrolyte is not purified scrupulously, the efficiency drops. Polyacetylene does not forgive casual handling and requires extreme care in the preparation of the electrochemical cell and electrolyte. Also, if initial oxidation is carried out to doping levels above about $y = 0.10$, the electrode potential enters the region in which the propylene carbonate electrolyte is increasingly unstable, and the oxidation/

reduction coulombic efficiency drops dramatically. An oxidation level of about $y = 0.10$, therefore, appears to be an upper limit for efficient cycling in the propylene carbonate electrolytes used in this work.

Oxidized polyacetylene appears to be unstable toward reaction with the propylene carbonate electrolyte. A sample oxidized to $y = 0.03$ lost about 40% of its stored charge during 40 h stand on open circuit.

Electrochemical reduction of polyacetylene

During the controlled potential reduction of polyacetylene in tetrahydrofuran containing 0.8M $LiClO_4$, little reaction takes place as the potential is decreased from 2.2 to 1.3 V. But, from 1.2 to 1.0 V the rate of doping increases rapidly. By 0.7 V the maximum doping level that can be achieved with high coulombic efficiency, $y = 0.09 - 0.10$, is reached. It may be possible to achieve higher levels by using a solvent/electrolyte salt combination that is more stable below 0.7 V.

When a number of reduction/oxidation cycles were carried out (reduction at 1.1 V followed by oxidation at 2.5 V), the characteristics of the polyacetylene electrode appeared to change. Initial currents upon polarization at 1.1 V were 4 - 5 mA/cm^2, on the basis of the geometric area of one side of the electrode, regardless of the cycle number. The current decreased to a plateau (0.75 - 1.2 mA/cm^2 in early cycles). The magnitude of the plateau decreased steadily with cycling. By the tenth cycle, it was in the range of 200 μA/cm^2. Because the average reduction current decreased with cycling, longer and longer times were required to attain a particular doping level.

During the controlled potential oxidations at 2.5 V, about 30 - 50% of the charge passed during reduction was recovered at current densities greater than 1 mA/cm^2 and about 60 - 70% of the charge was recovered at current densities greater than 0.1 mA/cm^2. Exhaustive oxidation until the current level was less than 2 μA/cm^2, which typically required 40 - 60 h, was required to attain an apparent coulombic efficiency, Q_{out}/Q_{in}, above 90%.

Polyacetylene that has been n-doped with Li^+ appears to be quite stable toward reaction with the THF/$LiClO_4$ electrolyte. For polyacetylene reduced to a y value of 0.04, near 100% coulombic efficiency was observed for 16 cycles if the film was oxidized immediately. If allowed to stand on open circuit for 24 h after reduction to $y = 0.04$, a slight decrease in efficiency to 95% was observed. For higher reduction levels, $y = 0.06 - 0.07$, the efficiency upon immediate discharge was 92 - 98%, and 76 - 88% after a 24 h delay.

5. Conclusions

On the basis of this and other research, polyacetylene does not appear to have major advantages over current electrodes for high energy density, rechargeable, non-aqueous electrochemical cells. It suffers principally from

instability, sensitivity to impurities, low volumetric energy density, and low-to-moderate gravimetric energy density.

Polyacetylene's instability and sensitivity to impurities clearly are problems for the manufacture of practical electrochemical cells. Polyacetylene is not a forgiving material. In the dry state, it is rapidly attacked by oxygen at moderate (>40 °C) temperatures. Polyacetylene that has been n-doped with Li^+ appears to be quite stable, but the p-doped compositions are unstable toward oxidation or halogenation of the double bond network comprising the polymer backbone. These irreversible oxidations proceed at relatively low temperatures with some dopants. Achieving high coulombic efficiencies for the oxidation of polyacetylene requires extraordinarily clean electrolytes.

Perhaps some oxidized forms, such as those containing ClO_4^- or AsF_6^-, are sufficiently stable to find application at low temperatures, and it may be possible to attain the degree of cleanliness necessary for the successful operation of a polyacetylene battery. Nevertheless, polyacetylene's instability and sensitivity to impurities are concerns that must be considered in any technological application of the material. The low-to-moderate gravimetric and low volumetric energy densities that can be achieved with either n- or p-doped polyacetylene are the result of the relatively low levels of doping that can be efficiently attained and the intrinsically low density of the polymer. The equivalent weight and density of $[CH(ClO_4^-)_{0.10}]_x$ are 229 g and about 0.5 - 1 g/cm^3, respectively. Corresponding values for $LiTiS_2$ are 118 g and 3.3 g/cm^3. $[Li_{0.10}CH]_x$ has an equivalent weight of 137 g, while that of Li is 7 g. It takes 8 - 12 times more volume to store the same charge in the form of Li-doped polyacetylene as in lithium metal.

Large-scale commercial development of polyacetylene for the purpose of creating a rechargeable battery with unusually high energy or power density seems of questionable value at this time. Nevertheless, a battery using polyacetylene as one or both electrodes could be made, and it is possible that its development would be justified for a specialized application.

Regardless of the present commercial outlook for polyacetylene, it is critical that fundamental research into its properties and those of other conducting polymers be continued. Polyacetylene is truly a revolutionary electrochemical material. That alone justifies its further exploration. In addition, the prospects for polyacetylene as a commercial, high energy density battery material might be much brighter if its stability were improved and maximum doping levels increased.

Acknowledgement

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