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COMPATIBILITY OF POLYACETYLENE WITH LITHIUM BATTERY MATERIALS. (U)

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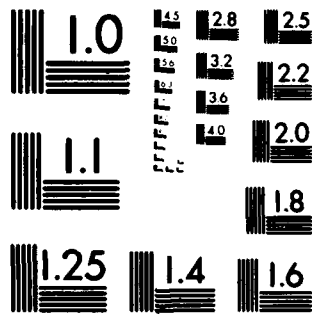
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COMPATIBILITY OF POLYACETYLENE WITH
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PREPARED FOR
THE U.S. NAVAL RESEARCH LABORATORY
UNDER CONTRACT NUMBER
N00014-82-C-2124

PREPARED BY
GEO-CENTERS, INC.
320 NEEDHAM STREET
NEWTON UPPER FALLS, MA 02164

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INTRODUCTION

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The object of the research conducted under this contract is to evaluate polyacetylene (CH_x) as a replacement for carbon as the cathode material in primary lithium/thionyl chloride (Li/SOCl_2) and lithium/sulfur dioxide (Li/SO_2) batteries. The choice of the Li/SOCl_2 inorganic electrolyte cell is based on the fact that it is the highest energy density system known to date.¹⁻² By itself, the favorable ratio of obtainable work to weight is not sufficient. For Navy applications, the rate at which the cell supplies energy - the power density - is very important. CH_x is a lightweight material with extremely high effective surface area ($60 \text{ m}^2/\text{g}$)³ and good electrical conductivity when doped, thus making it a good candidate for an electrode in a high power density cell.

↑
This report examines the stability of CH_x in the Li/SOCl_2 system and outline the approaches which are being investigated to improve the performance and stability of CH_x .

Results

1. Suitability of a CH_x Cathode in a Li/SOCl_2 Battery

Previous work has demonstrated that the electrochemistry of CH_x films involves a number of complex phenomena, including film structural reorganization,⁴ molecular isomerization⁵ and degradation. In addition, compatibility studies have shown that exposure of CH_x to SOCl_2 causes the silvery luster of the CH_x to turn white and the normally flexible films becomes brittle, indicative of oxidative decomposition.⁷ Although spectral, electrochemical and chemical analyses of CH_x and its breakdown products are still in progress, the prognosis for use of unmodified CH_x in a Li/SOCl_2 cell is not favorable.

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2. Stabilization of CH_x by Coating with Electroactive Polymers

The approach being taken to circumvent the problems of chemical and electrochemical degradation is to deposit an electroactive polymer coating on the CH_x substrate. The function of the coating is to provide physical protection of CH_x from the SOCl₂ solution and to mediate the transfer of reducing equivalents from the CH_x to SOCl₂. Electrochemical polymerization of transition metal complex monomers has been used successfully as a means of preparing uniform, electroactive films of a wide range of redox potentials in a reproducible, controlled manner.⁸ Polymerization can be initiated either oxidatively or reductively.

A number of polymerizable complexes of ruthenium have been synthesized, including: Ru(trpy)(bpy)(vpy)²⁺ (trpy = 2,2',2"-terpyridine; bpy = 2,2'-bipyridine; vpy = 4-vinylpyridine), cis-Ru(bpy)₂(vpy)₂²⁺, Ru(trpy)(vpy)₃²⁺, Ru(trpy)(BPE)₃²⁺ (BPE = trans-1,2-bis(4-pyridyl)ethylene) and cis-Ru(bpy)₂(py₂C₂)₂²⁺ (py₂C₂ = bis(4-pyridyl)acetylene). All of the above complexes undergo reductively-initiated polymerization; the BPE complex can participate in an oxidative film-formation reaction as well. (Note: the use of redox polymer films-composed of the metal complexes described above- for applications in secondary (storage) batteries constitutes a separate area of research which is also being explored.)

Ru(trpy)(vpy)₃²⁺ has been electropolymerized using AsF₅-doped CH_x as the electrode material. The resulting brown Ru-containing film was inhomogeneous and coated only a small part of the CH_x surface. The reason for the poor coating has been extensively attributed to electrochemical undoping of the CH_x (to the semiconducting state). As a result, uncompensated resistance through the CH_x film increases dramatically with consequent loss of potential control.

Further experiments along these lines are in progress to establish whether it is the complex or the nature of the reductive reaction which restricts the coating process.

The oxidative polymerization route will also be investigated using the $\text{Ru}(\text{trpy})(\text{BPE})_3^{2+}$ complex. The potentials required to deposit the metallopolymer are sufficiently positive of the formal potential of $\text{CH}_x^{+/\circ}$ that "undoping" (and loss of conductivity) should not inhibit the coating process.

Ru-modified CH_x films will continue to be examined by SEM to evaluate the uniformity of the coating; the electrochemistry and stability in non-aqueous solvents and SOCl_2 will be compared to that of uncoated CH_x .

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