COMPATIBILITY OF POLYACETYLENE WITH LITHIUM BATTERY MATERIALS (U)

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COMPATIBILITY OF POLYACETYLENE WITH LITHIUM BATTERY MATERIALS

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INTRODUCTION

The object of the research conducted under this contract is to evaluate polyacetylene (CH\textsubscript{x}) as a replacement for carbon as the cathode material in primary lithium/thionyl chloride (Li/SOCl\textsubscript{2}) and lithium/sulfur dioxide (Li/SO\textsubscript{2}) batteries. The choice of the Li/SOCl\textsubscript{2} inorganic electrolyte cell is based on the fact that it is the highest energy density system known to date.\textsuperscript{4} 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\textsubscript{x} is a lightweight material with extremely high effective surface area (60 m\textsuperscript{2}/g)\textsuperscript{5} 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\textsubscript{x} in the Li/SOCl\textsubscript{2} system and outline the approaches which are being investigated to improve the performance and stability of CH\textsubscript{x}.

Results

1. Suitability of a CH\textsubscript{x} Cathode in a Li/SOCl\textsubscript{2} Battery

Previous work has demonstrated that the electrochemistry of CH\textsubscript{x} films involves a number of complex phenomena, including film structural reorganization,\textsuperscript{4} molecular isomerization\textsuperscript{5} and degradation.\textsuperscript{7} In addition, compatibility studies have shown that exposure of CH\textsubscript{x} to SOCl\textsubscript{2} causes the silvery luster of the CH\textsubscript{x} to turn white and the normally flexible films becomes brittle, indicative of oxidative decomposition.\textsuperscript{7} Although spectral, electrochemical and chemical analyses of CH\textsubscript{x} and its breakdown products are still in progress, the prognosis for use of unmodified CH\textsubscript{x} in a Li/SOCl\textsubscript{2} cell is not favorable.

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2. **Stabilization of CH\textsubscript{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\textsubscript{x} substrate. The function of the coating is to provide physical protection of CH\textsubscript{x} from the SOCl\textsubscript{2} solution and to mediate the transfer of reducing equivalents from the CH\textsubscript{x} to SOCl\textsubscript{2}. 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.\textsuperscript{8} Polymerization can be initiated either oxidatively or reductively.

A number of polymerizable complexes of ruthenium have been synthesized, including: Ru(trpy)(bpy)(vpy)\textsuperscript{2+} (trpy = 2,2',2''-terpyridine; bpy = 2,2'-bipyridine; vpy = 4-vinylpyridine), cis-Ru(bpy)\textsubscript{2}(vpy)\textsubscript{2}\textsuperscript{2+}, Ru(trpy)(vpy)\textsubscript{3}\textsuperscript{2+}, Ru(trpy)(BPE)\textsubscript{3}\textsuperscript{2+} (BPE = trans-1,2-bis(4-pyridyl)ethylene) and cis-Ru(bpy)\textsubscript{2}(py\textsubscript{2}C\textsubscript{2})\textsubscript{2}\textsuperscript{2+} (py\textsubscript{2}C\textsubscript{2} = 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)\textsubscript{3}\textsuperscript{2+} has been electropolymerized using AsF\textsubscript{5}-doped CH\textsubscript{x} as the electrode material. The resulting brown Ru-containing film was inhomogeneous and coated only a small part of the CH\textsubscript{x} surface. The reason for the poor coating has been extensively attributed to electro chemical undoping of the CH\textsubscript{x} (to the semiconducting state. As a result, uncompensated resistance through the CH\textsubscript{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 Ru(trpy)(BPE)$_3^{2+}$ complex. The potentials required to deposit the metallopolymer are sufficiently positive of the formal potential of CH$_x^{+}$/O 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$_x$. 
References


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