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POLYMERIC MATERIALS FOR BATTER' APPLICATIONS

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The discipline of polymer science has experienced rapid growth in the last two decades. A large number of new polymeric materials with diverse characteristics and suitable for unusual applications have emerged. Among these polymeric materials, the electrical conducting polymer constitutes possibly a very important development in polymer science. These conducting polymers, by virtue of their atomic and microstructure, exhibit good electrical conductivity at room temperature, that arises from electronic and ionic mobility. The primary motivation behind the work with these materials is based on their potential technological applications that include rechargeable batteries, electrochromic devices, and sensors.

The polymer electrolyte lithium battery will possibly be the first commercial product to use ionic conducting polymers. In the last 10 years significant developments have taken place to screen, develop, and refine polymeric materials for the battery application. The purpose of this document is to review the state-of-the-art of polymeric materials for battery application and to recommend new frontiers of research that may lead to useful products for Aero Propulsion and Power applications.

A. ELECTRONIC CONDUCTORS

The 1970s saw considerable advancement in the development of conducting polymers, following the discovery of conducting films of polyacetylene, $(CH)_X$, by Shirakawa, et al.(1) and Ito, et al.(2). Subsequent research efforts of Shirakawa, et al.(3,4) resulted in further increases in the conductivity of polyacetylene by thirteen orders of magnitude. The enhanced conductivity was accomplished by doping polyacetylene with donor or acceptor type species. Conductivities of the order of 10^3 (ohm cm)⁻¹ were reported in doped polyacetylene. Although numerous other conducting polymers have been studied in the last two decades, doped polyacetylene remains the most conductive polymer.

A number of potential applications for doped polyacetylene polymers have been suggested, include antistatic coating, fuel cell catalysts, solar cells, photoelectrodes, and batteries. Since our primary interest involves batteries, subsequent discussion on polyacetylene will cover battery-related characteristics.

Three different types of batteries using polyacetylene have been explored:

1. <u>Polyacetylene as Anode</u>: The battery comprises a strip of $(CH)_x$ and lithium metal placed in the tetrahydrofuran (THF) solution of lithium naphthalide. The electrochemical reaction proceeds as expressed by Equation (1).

$$y(CH)_{x} + xy Li^{+}(Naph)^{-} \rightarrow (CH^{y-}Li^{+}y)_{x} + xyNaph.$$
 (1)

2. <u>Polyacetylene as Cathode</u>: The battery consists of $(CH)_X$ cathode with Li anode immersed in 1.0 M LiClO₄ in THF. The overall electrochemical reaction proceeds as expressed by Equation (2)

 $xLi + (CH)_{\chi} \rightarrow (Li^+CH^-)_{\chi}.$ (2)

3. <u>Polyacetylene as Both Cathode and Anode</u>: In the third type of battery, more highly doped $(CH)_x$ serves as a cathode and lightly doped $(CH)_x$ acts as an anode.

B. OTHER CONDUCTING POLYMERS

Numerous other organic polymers based on aromatic ring systems, such as polypyrrole, polythiophene, poly (p-phenylene) and poly (p-phenylene), exhibit electrical conductivity. However, conductivities of none of these polymers approach the conductivities of doped $(CH)_x [\cong 10^3 \text{ (ohm cm)}^{-1}].$

Figure 1 shows the structural formula of polyacetylene and other organic polymers. As such, these polymers are insulators. However, a transition occurs from insulators to conductors if these polymers are doped with p-type on n-type dopants. In addition, a number of derivatives of these polymers have also been synthesized and evaluated as conductors. For example, doped derivatives of polyacetylene include poly(diacetylenes), bis(aromatic suffoca)) diacetylenes, and poly(phenylacetylene).

The electronic conductivity of some of the insulating polymers can be raised by an incorporation of carbon or acetylene black in small amounts ($\approx 5\%$).

C. IONIC CONDUCTORS (POLYMER-SALT COMPLEXES)

An important class of electrical conductors is the polymer-salt complexes which are also termed polymer-ion electrolytes. The conduction mechanisms in the polymers discussed in the previous section involve soliton, polarons, and bipolarons, whereas the conductivity in the polymer-ion electrolytes to be discussed in this section is derived from ionic conduction. Furthermore, the electrical conductivities of the polymer-ion electrolytes are closer to the conductivities of semi-conductors, $[10^{-3}S \text{ cm}^{-1}]$ whereas doped organic polymer exhibits electronic conductivities as high as 10^2 S cm^{-1} .

The polymeric conducting electrolyte is formed by compounding a salt containing mobile ion and a polymeric material such as polyethylene oxide. In general, lithium salts are preferred and these include LiI, LiClO₄, LiSO₃CF₃, and LiBF₄. These salts may be complexed with poly(ethylene oxide), poly (propylene oxide), poly (epichlorohydrin), poly (ethylene succinate), poly (ethylene sulfide), and polyphosphazene. Figure 2 shows the backbone structure of some of these polymers.







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-O-CH₂-CH₂ Poly(ethylene oxide) CH₃ -O-CH₂-CH-Poly(propylene oxide)

CH₂Cl O-CH₂-CH-Poly(epichlorohydrin)

O-CH₂CH₂OC-CH₂CH₂-C-

Poly(ethylene succinate)

-S-CH₂CH₂-Poly(ethylene sulfide) -S-CH₂-CH₂CH₂-Poly(propylene sulfide)

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Figure 2. Backbone structures of various polymers.

The stoichiometry of the polymer salt complex varies. In the case of polyethylene lithium salt complex, stoichiometry and lithium ion concentration is defined by O/Li ratio. The stoichiometry is generally governed by the electrolyte requirements such as high conductivity, homogeneity, non-crystallinity, and stability.

Extensive research on polymer salt complexes has led to significant improvements in ionic conductivity at and below room temperature. The solvating polymers have been screened and designed to reduce crystallinity and obtain chain segments mobility that mediates enhanced ionic diffusion. Conductivity values in the range of 10^{-5} to 10^{-4} S cm⁻¹ at 25 °C have been reported by many groups. The ionic conductivity ($\approx 10^{-3}$ S cm⁻¹) is an important criterion for designing and developing new polymer salt complexes for battery applications. Another critical and equally important factor is the stability of the complexes that must be evaluated in a complete cell spanning a considerable period of time.

The electronic conductivity of the polymer salt complexes is of the order of 10^{-13} S cm⁻¹ at room temperature. The dielectric breakdown of a typical PEO-LiClO₄ film is $\approx 300,000$ V cm⁻¹. The data suggest the possibility of dielectric breakdown of the polymer electrolyte in an electrochemical cell (≈ 3 V) when the electrolyte thickness is close to 10^{-1} μ m. This value is almost two orders of magnitude lower than the electrolyte thickness being considered for battery applications.

Somewhat antagonistic requirements result from the diverse functions of polymer electrolyte in a rechargeable battery. Improved conductivity, chain mobility, elastomericity, and adhesiveness are difficult to reconcile with mechanical integrity, resistance, and reliability of 10-100 μ m films that are considered for battery applications. A compromise for these antagonistic requirements may be possible in ceramic-polymer or glass-polymer composites.

<u>Conductivity Mechanism</u>: The conductivity arises from ionic charge carriers in these polymer salt complexes. As the mobility of single valent ions having lower atomic weights tends to be higher, the choice of complexing compound is limited to alkali (lithium and sodium) salts. The general requirements for the complexing salts are low iattice energy and high propensity for complex formation. The complex formation is favored by alkali salts with large anions such as I⁻, ClO⁻4, SO₃CF⁻₃, and BF⁻4. The factors affecting the conductivity of the complex are temperature, crystallinity, homogeneity, and tendency for ionic pairing.

<u>Temperature Dependence</u>: The conductivity of these polymer-salt complexes exhibits moderate to strong temperature dependence. Many of these complexes show useful conductivities for battery applications above the ambient temperature. A nonlinear temperature dependence is generally observed as shown in Figure 3, which is reproduced from the work of Gauthier (5). At present, much of the research is directed towards enhancing the conductivities



- 1. PEO LiClO₄ (12/1) (1)
- 2. PEO Crosslinked LiClO₄ (8/1) (2)
- 3. PPO LiCF₃ SO₃ (9/1) (3)
- 4. Poly (ethylene adipate) $LiCF_3SO_3$ (4/1) (4)
- 5. Poly (ethylene succinate), $LiB\phi$ (6/1) (5)
- 6. Polyphosphazene ME7P, $LiCF_3SO_3$ (16/1) (6)
- 7. Polyphosphazene crosslinked IXMP LiCF₃SO₃ (32/1) (7)
- 8. Polysiloxane PMM57 linear LiClO₄ (25/1) (8)
- 9. Triol type PEO crosslinked with difunctional urethane $LiClO_4$ (50/1) (9)
- 10. PEO-PPO-PEO block copolymer crosslinked with trifunctional urethane LiClO₄ (20/1)
 - (10)

Figure 3. Temperature dependence of conductivity of selected polymer salt complexes.

in the -40 °C to \pm 40 °C range to make these polymer complexes a material of commercial value for battery pplications.

As stated in the previous paragraph, a typical plot of ρ versus 1/T of a polymer salt complex often features a curvature as shown in Figure 3. Such behavior can be quantitatively expressed by Equations (3) and (4). The parameter To of Equation (3) known as Vogel-Tamman-Fulcher (VTF) equation decreases continuously with an increase of the lithium salt in a polymer.

Equation (4) is the well known Williams-Landel-Ferry (WLF) equation allowing one to deduce transport property at a temperature T from the same parameters at temperature T'.

$$W_T = W_{T'} \cdot \exp C_1(T-T') / C_2 + T-T')$$
 (4)
ere.

where.

W _T	= reduced transport parameter
C1&C2	= composition dependent constant
Τ'	= arbitrary temperature

The equations are in fact equivalent $[C_1 = B/(T-T'), C_2 = (T'-T_0)]$ and they do not identify the diffusing species. The underlying assumption is that the concentration of mobile species remains constant throughout the temperature range of interest. Calculation of activation energy at different temperature regimes may provide insight into the basic diffusion mechanisms of charged species.

A quantitative representation of the transport phenomenon over a wide temperature range becomes a cumbersome task due to the existence of more than one phase in a given polymer salt complex. Several different types of crystalline and amorphous domains are often present in these complexes. In addition to the multiphasic character, the conductivity is also strongly ionic-salt-concentration dependent.

<u>Structure</u>: It has also been observed than an amorphous structure of the complex favors enhanced conductivities (6). As a result of this observation, efforts have been directed towards decreasing the crystallinity of solvating polymers such as polyethylene oxide (PEO) by incorporating crystallization inhibitors, plasticizers, and copolymers. Why would an amorphous structure favor enhanced conduction? Attempts have been made to answer this question on the basis of network chain length. It is believed that the diffusion of ionic species is mediated by the motion of the network chains. The motion of the network chains is size dependent and thus shorter chains (amorphous structure?) would favor enhanced ionic diffusion. Nonetheless, the answer lacks experimental evidence, and more fundamental research is needed to support the explanation.

The polymer salt complexes also exhibit reduction of conductivity whenever ion pairing occurs between the mobile alkali ion (cation) and the anion. Such ion pairing has been found in PEO-Li salts (7). The characterization of ion-pairing processes has been performed by molecular spectroscopy. Figure 4 shows a schematic illustration of the influence of ion pairing on ionic conductivity. One dimensional ion transport in the helical tunnel is prevented by ion pairing blocks. In the case of the three dimensional transport, the ion pairing does not block the ion transport. Figure 5 further illustrates the motion of ions in polymers. The polymer complexes are considered to be liquid-like in which the cationic motion is assisted by the large amplitude motion of network segments.

<u>Stability</u>: Mobility of diffusing species and their interaction with electrode materials in a battery using polymer electrolyte are limited and thus offer an advantage over the battery using liquid electrolyte. However, these solid electrolytes must remain stable during recycling and over a considerable period of time often in adverse environmental conditions. The polymer network must also resist degradation caused by the movement of diffusing species and any fatigue induced by environmental agents. Several analytical techniques such as cyclic voltammetry, infrared spectroscopy, and electron microscopy have been employed to assess the long-term stability of the polymer salt complexes. The cyclic voltammetry has emerged as the simplest and most useful technique for stability studies. However, the time span of the experiment seldom matches the long-term tests needed for battery cycling life.

D. PATENT LITERATURE

In the last 10 years, approximately 30 U.S. patents related to polymer electrolytes and electrodes have been granted. These patents cover a wide range of materials and processing techniques. Often the claims of these patents are broad, repetitious, and lacking in fundamental justification. This section will present a brief description of the issued patents and their relevance to our interest.

<u>U.S. Patent #4.303,748</u> issued December 1, 1981 relates to the fabrication of an electrochemical generator comprising an electrolyte constituted in part by a solid solution of an ionic compound dissolved in a macromolecular material. The ionic compound has a formula Mx, where M is an alkali metal or ammonium ion and x is an anion of a strong acid. The macromolecular material consists of homopolymers and copolymers derivative of several



Figure 4. Schematic illustration of influence of ion pairing on conductivity: (a) one dimensional ion transport and (b) three dimensional ion transport.



Figure 5. Schematic presentation of lithium ion migration in a small volume of polymer. The ion migrates from left to right which is assisted by large amplitude motion of the polymer that allows lithium to be 3 or 4 coordinated to oxygen atoms throughout the migration.

monomers comprising at least one heteroatom, notably oxygen or nitrogen, capable of forming donor-acceptor type bonds with cation M.

<u>U.S. Patent #4,357,401</u> issued November 2, 1982 describes an approach to produce a macromolecular material with desirable ionic conduction. The macromolecular material is derived from a crosslinked elastomeric complex mixed with one or more ionizable salts. The elastomeric complex is a propylene-polyoxide/ethylene polyoxide copolymer or an oxyethylated polyamine. The ionizable salts are of alkali metals, selected from among the salts of lithium, sodium, potassium, rubidium, and cesium.

<u>U.S. Patent #4,374,186</u> issued February 15, 1983 describes fabrication of a cell in which a cathode layer and anode layer are separated by a nonconducting ion-permeable layer and are sandwiched between a pair of conducting polymer layers. The conducting polymer layers and the ion permeable membrane form the cell. A liquid electrolyte is sealed in each compartment.

<u>U.S. Patent #4,505,997</u> issued March 19, 1985 relates to the formulation of novel ionic compounds that can be incorporated in polymers whose monomer units include at least one heteroatom such as oxygen or nitrogen. These heteroatoms form donor-acceptor type bonds with the cation of the ionic compound. The solid solutions thus formed can be utilized as an electrolyte of an electrochemical generator. The ionic compounds are represented by the formula $(C_n X_{2n+1} Y)_2 N^- M^+$ where x is a halogen, n varies from 1 to 4, Y is a CO or SO₂ group, and M is an alkali metal.

<u>U.S. Patent #4.517.265</u> issued May 14, 1985 describes formulation of anodic material comprising a mixture of ionically conducting macromolecular material and an alloy of lithium and carbon (Li_xC, where $0 \le x < 0.3$).

<u>U.S. Patent #4,542,081</u> issued September 17, 1985 relates to solid solutions constituted by one or several ionic compounds of the formula $(R-C=C)_4X^-M^+$ in which x is a trivalent element capable of entering into 4-coordination, the groups R are aprotic hydrocarbon radicals, and M is an alkali metal entirely dissolved in a macromolecular material. These solid solutions can be used as solid electrolytes for an electrochemical generator.

<u>U.S. Patent #4.556.616</u> issued December 3, 1985 also relates to systems of materials using ionic compounds incorporable and polymers of which the monomer units consists of at lead one heteroatom (oxygen or nitrogen) capable of forming bonds of donor acceptor type with the cation of the ionic compound. These solid solutions are useful for forming the electrolyte of an electrochemical generator. The ionic compounds are represented by the formula $[AlO_4(SiR_3)_4]^-M^+$ in which the groups R are aprotic hydrocarbon radicals and M is an alkali metal. <u>U.S. Patent #4,564,492</u> issued January 14, 1986 claims invention of a process for producing an oriented, crystalline poly(acetylene) in film or fibrous form by casting a polymer solution. The cast film is transformed into a poly(acetylene) film under tension or stress field in the temperature range of 20-200°C under reduced inert atmospheric pressure. Poly(acetylenes) are electronic conductors and may be useful for solid-state batteries.

<u>U.S. Patent #4,578.328</u> issued March 25, 1986 describes formulation of macromolecular materials comprising an ionic salt and copolymers of ethylene oxide and of a second monomeric unit the structure of which preserves the claim of a polyether structure. The use of the invention is in fabrication of composite electrodes and electrolytes of primary and secondary cells.

U.S. Patent #4,579,793 issued April 1, 1986 relates to the composition of a macromolecular material displaying ionic conduction. The material comprises a salt in solution in an organometallic polymer in which a metal atom is directly connected by the intermediacy of an oxygen atom to at least two of the organic polymer chains. The material is useful as an electrolyte.

<u>U.S. Patent #4.620.944</u> issued November 4, 1986 claims invention of ionic conducting macromolecular material. The material consists of an ionic salt dissolved in polyether solvent. The polyether is polycondensed and/or cross-linked and presents at least two chains connected to each other by a bridge that includes silicon/cadmium/boron/titanium and oxygen atoms.

<u>U.S. Patent #4.683.407</u> issued January 20, 1987 relates to the invention of an all solid state double layer capacitor and all solid state multicell electrochemical device. The electrolyte material of the device consists of a polymer such as polyethylene oxide containing an inorganic salt making the polymeric material ionically conductive.

<u>U.S. Patent #4,683.181</u> issued July 28, 1987 claims invention of an electrochemical generator consisting of an electrolyte made of macromolecular material and a positive electrode which includes a composite material. The composite positive electrode consists of a metallic compound to be reduced by the cation of the salt in the electrolyte. The electrolyte is constituted to a large extent by an amorphous polyether structure and possesses sufficient ionic conductivity at ambient temperature.

<u>U.S. Patent #4.720,910</u> issued January 26, 1988 relates to a method of preparing a cathode material. An insertion compound such as V_6O_{13} is ground and its particles are encapsulated in an electronic or ionic conducting polymers to form the cathode material.

<u>U.S. Patent #4.739.018</u> issued April 19, 1988 claims invention of a polycarbon sulfide derivative of general formula $(R_x CS_m)_n$ where R represents hydrogen or alkali metal or transition metal, x is the degree to which R is present in carbon sulfur structure, m is the degree of substitution with sulfur, and n is the number of units in the polymer chain. It is

claimed that the insertion of R is reversible, and intended applications include electrode materials.

<u>U.S. Patent #4,742,127</u> issued May 3, 1988 relates to the invention of polycarbon sulfide derivatives comprising units of $(R_x CSm)_n$ in which R represents hydrogen, an alkali metal, or a transition metal; x is the fraction of R; m is the fraction of sulfur substitution; and n is the number of units. The insertion of R in the formula is claimed to be reversible. A similar patent (#4,739,018) had been granted to the same inventors on April 19, 1988.

<u>U.S. Patent #4,748,542</u> issued May 31, 1988 describes an invention of a solid-state electrochemical device. The electrolyte material employed in the device consists of an ionically conductive polymer complex such as polyethylene oxide mixed with an inorganic salt.

U.S. Patent #4,753,715 issued January 28, 1988 relates to electropolymerization at pyrrole, thiosphene, and furan films. These conducting films with high surface-specific capacity and favorable kinetics can be used as electrode materials in galvanic storage batteries. The films are deposited by flowing primary anodic current from an aqueous or organic solution of monomer in the presence of conducting salts.

<u>U.S. Patent #4,758,483</u> issued July 19, 1988 relates to the invention of an amorphous, single phase, solid polymeric elelectrolyte comprising a solution of ionic compound in a macromolecular material. The ionic compound is dissolved in a copolymer of ethylene oxide and a second polymer such that the copolymer chain maintains a polyether characteristic. The patent also claims fabrication of high performance composite electrode embodying this electrolyte.

<u>U.S. Patent #4,781,443</u> issued November 1, 1988 claims invention of an electronically conducting organic material for use on battery electrodes. The organic material consists of at least one π -conjugated linear unit as its backbone, optically doped with an n-or p-type dopant. An example of the material is poly(2,2'-dipyrryl methane) doped with CF₃SO₃ ions which is claimed to be relatively air and water-stable with a conductivity of about 1.0 S cm⁻¹.

<u>U.S. Patent #4,792,504</u> issued December 20, 1988 claims invention of a solid polymeric electrolyte consisting of a continuous network of a crosslinked polyethylene oxide containing an ionic conducting phase that includes a metal salt and dipolar apotic solvent.

<u>U.S. Patent #4,803,249</u> issued February 7, 1989 is very similar to US patents #4,739,018 and 4,742,127 except that this patent has a different number of claims on synthesis of polycarbon sulfide derivative comprising $(R_x CSm)_n$ units. The definition of symbols has been presented earlier.

U.S. Patent #4,818,644 issued April 4, 1989 relates to an invention of ionically conducting material dissolved in a solvent and characterized by the fact that the salt is represented by the following formulae



<u>U.S. Patent #4.830,939</u> issued May 16, 1989 relates to an invention of a method for producing interpenetrating polymeric network containing liquid electrolyte for use in a solid-state electrochemical cell. The polymeric network is formed using a mixture of radiation polymerizable monomeric liquid, a radiation inert ionically conducting liquid, and an ionizable alkaline metal salt. The mixture is subjected to active radiation to cross-link radiation polymerizable ionically conducting material.

<u>U.S. Patent #4,832.869</u> issued May 23, 1989 claims invention of highly conducting polymers and materials for polymeric batteries useful for spacecraft and other applications. The invention describes a number of conductive organic polymers having an electrical conductivity greater than 10^{-2} ohm⁻¹cm⁻¹. The structures of the organic polymers contain heteroatoms such as oxygen, nitrogen, and sulfur which are found in alkylene, aralkyl, and aryl groups. In addition, organic and inorganic dopants have been suggested for enhanced conductivity.

<u>U.S. Patent #4.851.307</u> issued July 25, 1989 reports invention of an ionically conducting material consisting of a salt and solvent. The solvent consists of a sulfonated derivative of formula R_1R_2N -SO₂NR₃R₄, where R_1 , R_2 , R_3 , and R_4 are each independently a

 C_{1-10} oxalkyl group. The ionically conducting materials are claimed to be useful for producing electrochemical generators.

<u>U.S. Patent #4,882,243</u> issued November 21, 1989 describes an invention of ionconducting solvent-free polymeric systems characterized as being cationic single ion conductors. The polymer electrolytes comprise a flexible polymer backbone to which a metal salt of lithium, sodium, and potassium is attached. The solid electrolyte may be prepared either by attaching the hindered phenol directly to a flexible polymeric backbone, followed by neutralization of phenolic OH's or by reacting the hindered phenol with a polymer precursor which is then polymerized to form a flexible polymer having phenolic OH's that are subsequently neutralized. The ionic conductivity of these solvent free polymer electrolytes was reported to be in the range of 10^{-4} to 10^{-7} S cm⁻¹ at room temperature.

E. CONCLUDING REMARKS

It is apparent that significant interest exists in the development of polymeric materials for battery applications. The motivation is driven by the possible development of potentially high-energy density, high cyclability, large-scale manufacturability, environmentally safe, and small weight batteries. Obviously these developments are likely to influence the Aero Propulsion and Power system design and development. Thus, it is felt to be in the interest of the Air Force to nurture this developing technology, and when solid-state, polymeric, rechargeable batteries become commercially available, the Air Force will be better prepared to make a balanced decision with regard to their procurement and use in Aerospace power systems.

Several potentially important frontiers of research have been identified. These research areas relate to the design and development of anodes, cathodes, and electrolytes and they are briefly outlined as follows.

ANODES

Problems:	Dendrite growth of lithium leading to current leakage and short circuitry.
Future Research:	(1) Conduct studies and evaluate lithium alloys such as Li-B, Li-Ga, etc.
	(2) Investigate and understand dendritic growth process
	ELECTROLYTES
Problems	(1) I ow room temperature conductivity

r routents.	(1) Low room temperature conductivity
	(2) Strongly temperature dependent conductivity
	(3) Mechanically weak
	(4) Chemically unstable
Future Research:	(1) Investigate new polymeric systems
	(2) Understand and explain mechanism of ion transport and role of
	polymer structure
	(3) Evaluate aging studies of selected polymers
	(4) Investigate composite materials
	CATHODES
Problems:	(1) Poor reversibility
	(2) Problems related to lithium insertion

Research Topics: (1) Assess $Fe_2O_3-V_2O_5$ glasses as cathode materials

(2) Evaluate polymer vanadium oxide composite

The Battery Laboratory is uniquely equipped with facilities and equipment to pursue a few selected and relevant research topics. The results of these research efforts will contribute to the advancement of the state-of-the-art of solid state polymeric battery technology and development of in-house research expertise.

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