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Journal of Power Sources 96 (2001) 337–342

JOURNAL OF
**POWER
SOURCES**

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On the origin of conductivity enhancement in polymer-ceramic composite electrolytes

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Received 1 September 2000; accepted 7 November 2000

Abstract

This paper analyzes thermal history dependent conductivity data of a PEO:LiBF₄-TiO₂ (20 wt.%) electrolyte to understand the origin of conductivity enhancement in polymer-ceramic composite electrolytes. The polymer-ceramic composite electrolytes are proposed to comprise of an assemblage of molecular dipoles whose orientations are dependent upon temperature, prior thermal history, and electric field. One of the major factors contributing to the conductivity is the orientation of these dipoles. Oriented dipoles augment conductivity; however, thermal energy at higher temperatures tends to randomize their orientation. A specimen cooled rapidly from high temperature exhibits low conductivity, and if held isothermally its conductivity increases with time. The conductivity enhancement has been attributed to the ordering of dipole moments. A reduction in conductivity as a function of time may also be observed in these electrolytes, which is attributed to crystallization of the polymer phase. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Composite; Electrolyte; Ionic conductivity; Dielectric constant; Dipoles

1. Introduction

A variety of dielectric materials, such as polymers, glasses, ceramics, and their combinations, may be useful as solid electrolytes for high energy density lithium rechargeable batteries. Among these materials, polymers have received considerable attention in the last two decades because of their low density, manufacturability, and capacity to accommodate volume changes as compared to true rigid, inorganic solid electrolytes. The subject of polymer electrolytes has been extensively covered by review papers and a monograph [1,2]. Inorganic solids and glasses as electrolytes have also received significant attention [3,4] but to a lesser degree.

A material derived from polymer and ceramic phases is identified as a polymer-ceramic composite in this paper. This composite type of material with significant ionic conductivity thus becomes a subset of solid electrolytes and has recently received considerable attention. Two review papers [5,6] have been published on the topic in the last 5 years. An analysis [7] of a broader range of composite electrolytes reveals that the incorporation of ceramic components in a polymer matrix leads to enhanced conductivity, cationic transport number, and electrode electrolyte interfacial stability.

The conductivity, σ , of electrolytes from the polymer-ceramic composite PEO:LiBF₄-TiO₂ [8] and PEO:LiBF₄-ZrO₂ [9] systems is dependent upon heat treatment parameters such as temperature (50–150°C) and time (soak time and heating and cooling rates). In general, higher temperatures and longer heat treatments followed by a slow cooling rate enhance conductivity. The enhancement in conductivity may approach four orders of magnitude at subambient temperatures. It has been proposed that the enhancement in conductivity is related to a new transport mechanism which develops due to an interaction of the polymer and ceramic phases [9]. Furthermore, a conductivity relaxation which appeared to be a characteristic of these composite electrolytes was proposed to be related to the melting and crystallization of PEO. The purpose of this paper is to further analyze previously reported [9] experimental data and develop a better understanding of the heat treatment effects and the origin of the conductivity enhancement.

2. Experimental

The PEO:LiBF₄-TiO₂ composite electrolyte films were made by the solvent casting technique using reagent grade poly(ethylene) oxide (PEO), lithium tetrafluoroborate (LiBF₄), and nanosize titanium oxide (TiO₂). The [O]:[Li]

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ratio of the polymer complex was 7.73:1, and the average particle size of the TiO_2 was 21 nm. A solution of PEO (Union Carbide, 300,000 mol wt.) and LiBF_4 in AR grade acetonitrile (Aldrich) was prepared in which TiO_2 was dispersed and sonicated. After sonication, a homogenized colloidal solution was obtained which was cast and dried into a film form of about 100 μm thickness.

The conductivity measurement was carried out using an EG&G impedance spectrometer model 398 in the frequency range from 0.1 Hz to 100 kHz with stainless steel (SS)/composite electrolyte/SS cells. The cells were contained in a glass vessel which was heated in a temperature bath to the set temperature maintained within $\pm 1^\circ\text{C}$.

3. Results and discussion

3.1. Conductivity data

A specimen in blocking electrode configuration was heated to 150°C , held at this temperature for 30 min, and

then rapidly cooled to 0°C . The conductivity of this specimen was measured as a function of temperature and time while the temperature was raised from 0 to 150°C . The experimental data are shown in Fig. 1. At each temperature there are two data points, an arrow, and a number of hours. The data points represent the range of conductivity values, the arrow pointing upward indicates conductivity enhancement, and the number of hours is the time interval between the two measured values of conductivity. For example, at 0°C , after the specimen was cooled from 150°C , the $\log \sigma$ was -9.85 . The $\log \sigma$ increased to -9.37 after it was held at the temperature for 114 h. This type of conductivity enhancement appears at all temperatures; however, the degree of enhancement, as measured by the absolute difference between the two data points and normalized for the hold time, diminished as the temperature was raised from 0 to 150°C .

The specimen whose thermal history and conductivity data are shown in Fig. 1 was equilibrated for 30 min after it reached 150°C , and then cooled down gradually and slowly

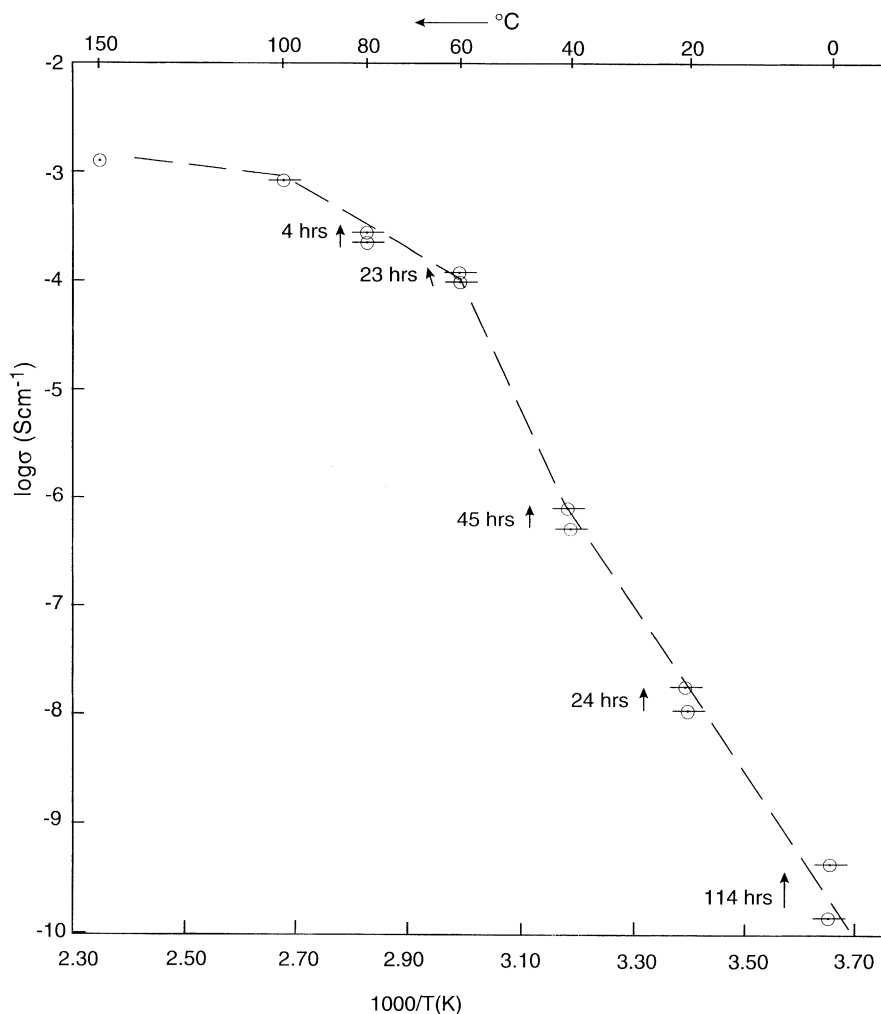


Fig. 1. Conductivity of PEO: LiBF_4 - TiO_2 (20 wt.%) composite electrolyte during heat-up. The specimen was heat treated at 150°C for 30 min and then quenched to 0°C .

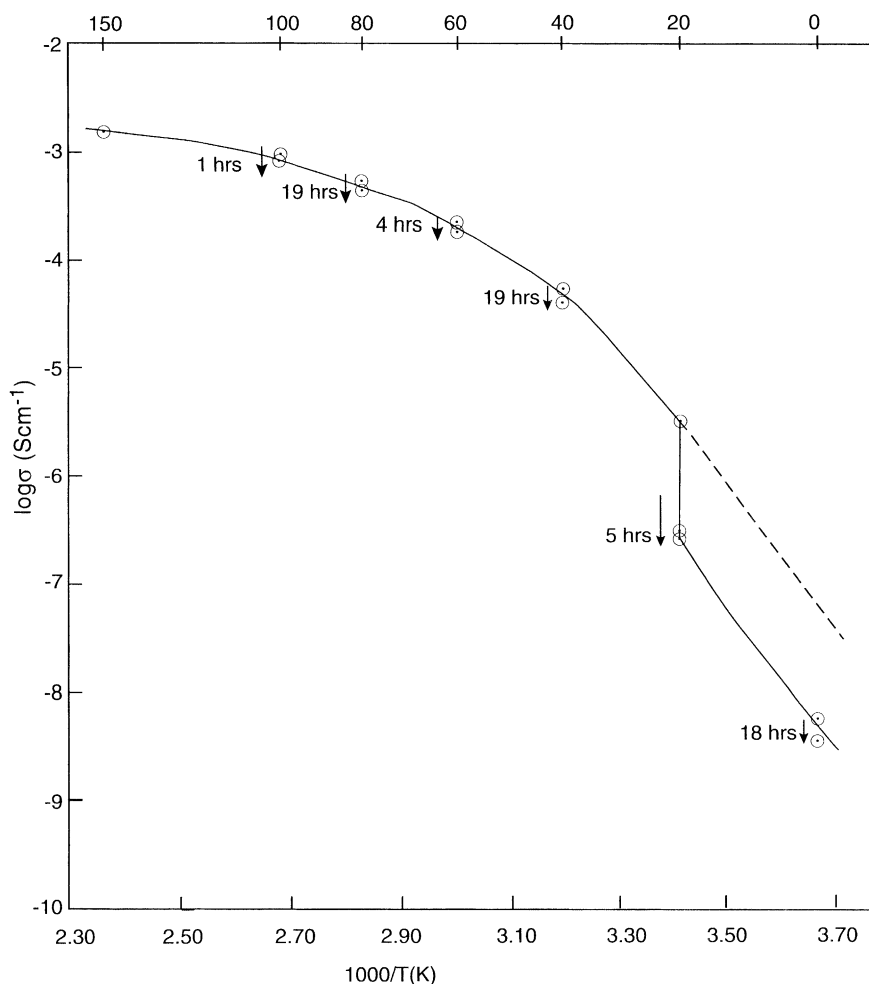


Fig. 2. Conductivity of PEO:LiBF₄-TiO₂ (20 wt.%) composite electrolyte heat treated at 150°C for 30 min. The conductivity was measured while the specimen was slowly cooled from 150°C and stabilized at the temperature of measurement.

to 100, 80, 60, 40, 20, and 0°C for conductivity measurement. The conductivity values and hold time at each of the temperatures are shown in Fig. 2. In general, the conductivity decreased as the hold time increased at the given temperature. The conductivity variations as a function of hold time at all temperatures above 20°C were small but measurable and significant. However, the decline in conductivity at 20°C is pronounced. The conductivity decreased more than an order of magnitude in the first 2–3 h, and comparatively subsequent reduction was small. If the first data point at 20°C is taken as the measured value, this conductivity curve is comparable to data reported by Croce et al. [10] on TiO₂-containing composite electrolytes.

3.2. Dielectric constant and conductivity relationships

The dielectric constant, κ , is related to the polarization, P , and local electric field, E_L , through Eq. (1)

$$\kappa = 1 + \frac{P}{\epsilon_0 E_L} \quad (1)$$

where ϵ_0 is the permittivity of free space.

Furthermore, it can be demonstrated [11] that the second term of Eq. (1) is related to the number of dipoles, n , through Eq. (2)

$$\frac{P}{\epsilon_0 E_L} = \frac{nz^2 e^2 b^2}{4kT} \quad (2)$$

where z is the valence, e the electron charge, b the distance between potential wells, k the Boltzmann constant, T the temperature.

Substitution of Eq. (2) in Eq. (1) leads to an expression, Eq. (3), relating κ and n

$$\kappa = 1 + \frac{nz^2 e^2 b^2}{4kT}. \quad (3)$$

Eq. (3) establishes a relationship between the number of dipoles, n , and dielectric constant, κ . Other parameters of the equation except temperature, T , are essentially constants. Ceramics as a class of materials possess a higher dielectric constant, 10–1000 as compared to polymers. A solid composite material which is a mixture of polymer and ceramic phases thus possesses a dielectric constant gradient at a microscopic level. The dielectric constant gradient is

proposed to be the origin of polymer dipole and ceramic dipole interaction.

An expression for conductivity, σ , in a solid as derived from basic principles [11] is given by Eq. (4)

$$\sigma = \frac{n' \alpha v z^2 e^2 b_i^2}{2kT} \exp\left(-\frac{\Delta H}{RT}\right) \quad (4)$$

where n' is the number of charge carriers, α the accommodation coefficient, v the vibration frequency of charge carriers, ΔH the activation energy, R the gas constant, b_i the distance between potential wells for ionic conduction.

The conductivity data discussed earlier deals with a material in which the major variable, the number of charge carriers, n' , remains constant.

The dielectric constant, κ , of PEO:LiBF₄ complex (≈ 5) may be locally influenced by the neighboring TiO₂ particles. The κ of TiO₂ is anisotropic and possesses values of 170 and 86 in two primary directions. The high κ of TiO₂ is primarily related to the existence of a large number of dipoles which result from lack of symmetry of its crystal structure. Such a large difference in the dielectric constants between the PEO:LiBF₄ complex and TiO₂ leads to an inductive effect in which the PEO polymer chain must compensate for TiO₂ dipole moment locally. This scenario requires chain rotation and stretching to raise the local dielectric constant of the polymer complex. The concept is physically illustrated by Fig. 3(a)–(d). The helical structure of PEO is shown in Fig. 3(a). The dipole moments (arrows) associated with molecular groups of a section of the helix are shown in Fig. 3(b). The energy for rotation of the C–O and C–C bonds is 6.3 and 12.6 kJ, respectively. The low energy of rotation around the C–O bond allows its interaction and reversal of the dipoles orientation when a TiO₂ dipole, as shown in Fig. 3(c), is brought in close proximity. The resultant dipole orientations

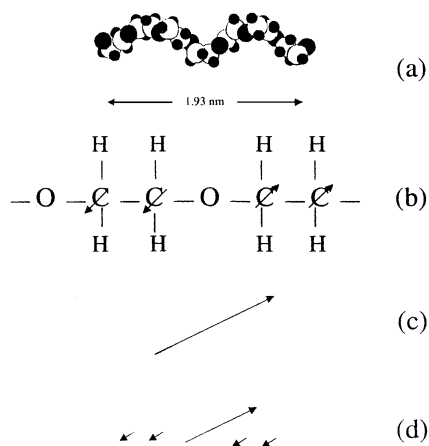


Fig. 3. (a) Poly(ethylene) oxide, PEO structure viewed parallel to the axis of the helix. The black and white circles represent oxygen and carbon atoms, respectively. Hydrogen and lithium atoms are not shown. (b) Dipole moments (small arrows) associated with molecular groups of PEO polymer chain. (c) Dipole moment of TiO₂ crystallite. (d) Interaction and reversal of dipoles when a section of polymer chain (shown in (b)) and TiO₂ crystallite (shown in (c)), are in close proximity.

are shown in Fig. 3(d). This phenomenon is reflected by time and temperature dependence of conductivity and is believed to be the origin of conductivity enhancement. The dipole interaction and its effect on conductivity are pronounced at low temperatures because the thermal energy to randomize dipole orientation is minimized while the polymer matrix is rigid, preventing disorientation of dipoles.

3.3. Particle characteristics, dipole orientation, and frictional force

The interaction energy, E , of dipoles of polymer chains and TiO₂ crystallites with the local electric field, E_L , is given by

$$E = -\mathbf{p} \cdot E_L \quad (5)$$

where \mathbf{p} is the dipole moment.

The interaction energy of the dipole tends to orient the moment parallel to the field. If the dipoles behave independently of each other, such as in gases and fluid media, the resulting orientation is limited by thermally-induced disorder. The probability $\rho'(\theta)$ of finding a dipole at an angle θ to the field E_L is given by the Boltzmann statistics

$$\rho'(\theta) \sim e^{-E/kT} = e^{pE_L \cos \theta / kT} \quad (6)$$

Eq. (7) approximates polar liquid and gases reasonably well. However, for solids a strong interaction between dipole and its neighbors exists. The interaction hinders free rotation of dipoles and may suppress it completely. For solids such as the PEO:LiBF₄-TiO₂ composite electrolytes it can be shown [12] that the average component of the dipole moment parallel to the field is

$$\bar{p}_{\parallel} \approx \frac{p^2 E_L}{3kT} \quad (7)$$

The oriented dipoles either resulting from an applied dc field or due to a reduction in the thermal energy (kT) will remain relatively unperturbed in the rigid polymer matrix. The decay of dipole orientation is resisted by the friction factor for rotation, ξ , of highly viscous polymeric medium [13], and can be approximated by Eq. (8)

$$\xi = 8\pi\eta a^3 \quad (8)$$

where η is the viscosity, a the radius of spherical TiO₂ particles.

If the TiO₂ particle behaves like a rigid ball tending to rotate due to an applied electric field or thermal energy in a viscous polymeric medium [13], the relaxation time, τ , can be expressed by Eq. (9)

$$\tau = \frac{4\pi a^3 \eta}{kT} \quad (9)$$

Eq. (9) is revealing with respect to the influence of the TiO₂ particle radius, polymer viscosity, and temperature on the relaxation time. If the TiO₂ particle radius is increased from

10 to 100 nm, the relaxation time increases by three orders of magnitude — leaping from seconds to weeks. The conductivity relaxation under discussion would not be observed with micron size TiO_2 particles using the conductivity measurement technique of this study. The viscosity of the polymer and temperature affect the conductivity relaxation but their impact is not as pronounced as the particle size.

3.4. Electroactive components and their contributions

The molecular structure of the PEO: LiBF_4 complex and nanosize crystallites of TiO_2 possess permanent dipole moments, and these dipoles are electroactive and may be considered as the building blocks of the composite electrolyte. On a microscopic level, the κ of the polymer phase and the conductivity is greatly increased by the orientation of the polymer dipoles resulting from an interaction with neighboring TiO_2 dipoles. At higher temperatures, the dipoles are randomly oriented because of the thermal energy of polymer chains and TiO_2 crystallites and the bulk electrolyte possesses a zero net moment. At lower temperatures, ordering of these dipoles are energetically favorable while retaining zero net moment of the electrolyte. The dipolar polarization of the electrolyte is thus expected to be strongly temperature and cooling rate dependent. The electric field will align them because the dipole-electric field interaction energy is negative and it lowers the energy of the system. The degree of dipole orientation constraint varies with viscosity and temperature of the electrolyte. At the high temperature end ($\approx 100^\circ\text{C}$) and above the melting point of PEO, the liquid-like structure allows rotation of dipoles; but as the temperature is lowered, the dipole rotation is severely restricted. This leads to thermally frozen, nonequilibrium orientations of dipoles, and if such an electrolyte is isothermally stabilized, the dipole tends to orient in a low energy, equilibrium configuration. The concept is schematically illustrated in Fig. 4(a) and (b).

The conductivity data of the PEO: LiBF_4 - TiO_2 (20 wt.%) composite electrolyte as shown in Fig. 1 exhibits a relaxation at each temperature in which conductivity increases. It is proposed that thermally frozen, nonequilibrium, and randomly oriented dipoles tend to approach an equilibrium, oriented configuration — a structure conducive for enhanced conductivity. The transition from nonequilibrium to an equilibrium state is slow because it takes place in an amorphous, highly viscous polymer medium. As the temperature is raised, the degree of conductivity relaxation or enhancement diminishes because of the negative influence of thermal energy.

During a slow cool down, the conductivity remains high, Fig. 2, because the thermal energy (kT) disrupting the dipole orientation is reduced and the permanent dipoles have more time to transition into an ordered state. At 20°C , a precipitous drop in conductivity occurs. The drop is attributed to the crystallization of the polymer component, which has been confirmed by DSC measurements and reported earlier [9].

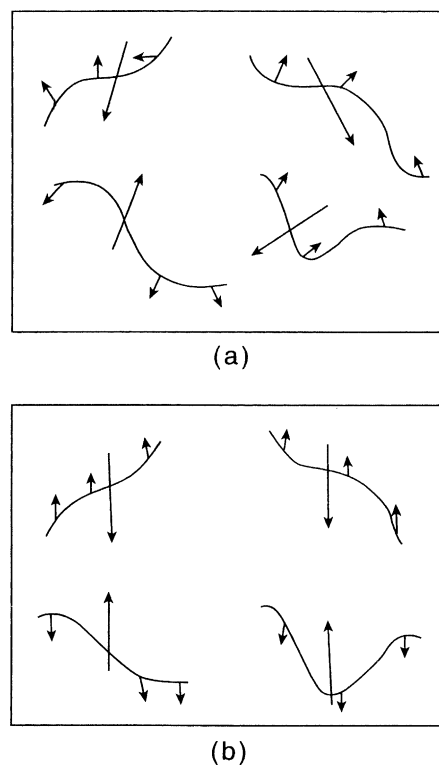


Fig. 4. (a) Orientation of dipoles associated with polymer chains and TiO_2 particles in a composite electrolyte which has been rapidly cooled. Small (associated with polymer chain) and large arrows represent dipoles associated with PEO: LiBF_4 complex and TiO_2 , respectively. The magnitudes of dipole moments were schematically given a 3:1 ratio. (b) Thermal stabilization (annealing) orders dipole orientations.

It is evident that the size of the TiO_2 particles is critical. Larger particles in the polymer matrix will remain randomly oriented and contribute little to the conductivity through the dipolar alignment. Nonetheless, these large TiO_2 particles will impede crystallization of PEO below its melting temperature and in an indirect manner contribute to the conductivity by maintaining an amorphous polymer structure.

The medium of transport remains and population of conducting ions resides in the polymer phase. However, these basic attributes critical for improved conductivity of an electrolyte are compromised when the fraction of TiO_2 particles is increased beyond an optimum limit. Furthermore, at higher concentrations of TiO_2 , inter-particle interaction may lead to aggregation of particles and blockage of the conduction path. These considerations point out that an optimum concentration of ceramic phase yields the highest conductivity values in a polymer-ceramic composite electrolyte [5].

4. Summary and conclusions

Analyses of temperature-dependent conductivity data in the PEO: LiBF_4 - TiO_2 (20 wt.%) system reveal that the conductivity enhancement is related to the presence of TiO_2

particles because they retard crystallization of the polymer phase and at the same time affect the local structure through dipolar interaction. The significant conclusions of the analyses are summarized as follows.

1. The conductivity of a composite electrolyte, when monitored under isothermal conditions for a prolonged time, may increase or decrease depending upon prior thermal history and the nature of the structural transition at the given temperature.
2. The TiO₂ particles in the composite electrolyte exist as a permanent strong dipole whose orientation depends upon the temperature and thermal history of the specimen. The oriented dipoles yield higher conductivity. The heating and cooling rates have an influence on the dipole orientation and conductivity.
3. The conductivity enhancement originates from an interaction of the dipoles associated with the polymer containing conductive ions and TiO₂ phases.
4. The TiO₂ particles retard crystallization of PEO when the molten composite electrolyte is cooled from a temperature above its melting point. The TiO₂ particles also preserve the amorphous structure, but the polymer may recrystallize if held for a long time at an appropriate temperature.
5. The particle radius of TiO₂ is critical; increasing the radius by an order of magnitude increases the relaxation time from seconds to weeks.
6. The existence and retention of a liquid-like or amorphous structure is not a sole criterion for conductivity enhancement. It is proposed that thermal treatments augment and preserve the amorphous structure and also develop a preferred conduction path through dipolar interaction.
7. The polymer phase remains the medium of transport and reservoir for conducting ions. The TiO₂ additive

facilitates the transport through a localized influence on the polymer chain conformation.

Acknowledgements

B. Kumar gratefully acknowledges financial support by the Air Force Research Laboratory, Propulsion Directorate, under Contract No. F33615-93-C-2350. The authors express their appreciation to Mrs. L. Lucente for conducting the experimental work and to Mr. R.A. Marsh for his continued support and encouragement.

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