PRACTICAL TOPICS PAPER

THE ROLE OF ELECTRICAL INSULATION IN ELECTROCHEMICAL DEGRADATION OF TERRESTRIAL PHOTOVOLTAIC MODULES

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ABSTRACT

In this paper, electrochemical degradation of photovoltaic modules - encapsulated solar cells - is explored. It is pointed out that both device and insulation properties must be considered in determining the overall performance and remaining life of the system. A quantitative correlation between field-exposure time and exposure time in accelerated multistress tests is developed, based upon the concept that equal quantities of leakage current charge transfer between cells and module frame results in equivalent electrochemical damage. The correlation is useful in interpreting accelerated test data. The effects of temperature, humidity, and applied voltage difference on the quantity and rate of cell-frame charge transfer and, hence, on electrochemical degradation are documented. Experimental data indicate that cell-frame polarity also influences the nature and severity of electrochemical degradation. These effects are regarded individually and collectively, and lead to a comprehensive understanding of electrochemical degradation processes in photovoltaic systems.

INTRODUCTION

The role that dielectric materials play in the isolation and containment of electrical charge and current has been recognized and studied as long as electricity itself [1,2]. It is known that, for encapsulated dc circuitry, the greater the electrical conductance of the insulating dielectric, the greater the leakage of charge from the circuitry through the insulation to ground. If, as generally occurs, the conductance of the insulation increases over the lifetime of the device, leakage currents may eventually reach unacceptably high levels, at which time the insulation may be said to have failed to perform its function of electrical insulation. This mode of failure is not the catastrophic failure associated with electrical overstress resulting in the immediate formation of a zero-resistance path through the insulation. Rather, it is a low-stress phenomenon generally associated with the influx into the encapsulation of water, or with the effects of elevated temperature or ultraviolet irradiation, which accelerate naturally occurring processes such as electrode dielectric interactions (electrochemistry) and charge migration (diffusion). Because no zero-resistance breakdown paths form, a definition of insulation failure remains elusive. However, such processes do result in degradation of device performance, and a suitable definition of failure must consider the condition of the device in addition to the condition of the insulation.

The device under consideration in this paper is a solar cell. Strings of solar cells are encapsulated into modules, modules are wired to form panels, and panels are wired to form arrays as illustrated in Fig. 1, which presents the basic photovoltaic nomenclature.

Briefly, a solar cell works as follows: Light penetrates the solar cell, effecting a separation of positive and negative charge carriers at the p-n junction. This constitutes a real current that is collected by the top-surface metallization for delivery to the power-conditioning equipment (dc to ac converters) and the network or load.

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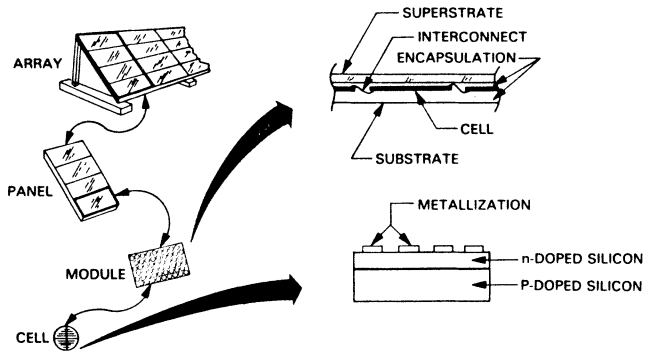

Fig. 1: Photovoltaic Array Nomenclature

Modern cell metallization systems include Ag paste, Ti-Pd-Ag (passivated silver, or tri-metal), and Ni-systems (Ni-Sn, Ni-Pb-Sn, Ni-Cu-Sn, and Ni-Pd). Most of the currently favored module encapsulants are solid, transparent polymers: ethylene vinyl acetate (EVA), polyvinyl butyral (PVB), and silicone rubber (RTV). These polymers bond the cells to the glass superstrate and are generally protected on the rear side by a substrate film such as Tedlar®.

The key focus of photovoltaic reliability research at the Jet Propulsion Laboratory (JPL) is achieving 30-year module life. This is complicated by the fact that modules have been deployed terrestrially for only 8 to 10 years, so there exists no direct knowledge about failure mechanisms active in a 10-to 30-year time frame.

To identify long-term failure mechanisms, photovoltaic modules have been subjected to various tests including accelerated temperature/humidity (T/H) environments at Wyle Laboratories for up to 480 days [3,4]. Many degradation phenomena have been observed, including optical transmission losses in the encapsulation and the dissolution and migration of electrode material - i.e., cell metallization - throughout the encapsulation, a phenomenon referred to as electrochemical degradation. This phenomenon has been identified as a potential long-term reliability problem and a series of refined experiments have been conducted to determine degradation rates and build a data base from which reliable life prediction capability can be established. These experiments are multistress tests involving exposure to accelerated levels of temperature, humidity, and voltage. This paper reports some results of these experiments, establishes the role of electrical insulation in photovoltaic device electrochemical degradation, presents a status report on our present understanding of the electrochemical degradation mechanism, and reviews our present ability to predict photovoltaic device service life.

ELECTROCHEMICAL CORROSION AND PHOTOVOLTAIC DEVICE LIFE

An algorithm for predicting yearly average module failure rates has been presented in [5]. That algorithm, based upon measured median cell failure rates, an assumed log-normal cell failure distribution, and reduced solar radiation surface meteorological observations (SOLMET) weather data, will not be further developed here. Instead, data from various electrochemical degradation experiments will be presented and interpreted to shed more light on photovoltaic device electrochemical degradation rates and mechanisms and on the crucial role played by the dielectric.

The Electrochemical Degradation Mechanism

The particular module degradation mechanism addressed in this paper is electrochemical degradation, i.e., the degradation resulting from electrode-dielectric interfacial interaction. A schematic, qualitative representation of the mechanism is depicted in Fig. 2. As conceived [5], exposure to high temperature, humidity, and voltage difference between two electrified cells, or between an electrified cell and grounded frame, may result in dissolution of cell metallization material into the surrounding encapsulant. Driven by voltage and concentration gradients, the dissolved metallization ions diffuse through the encapsulant (wavy arrows, Fig. 2) to the cathode where they deposit to form metallic dendrites. These "grow" back toward the anode until the intervening encapsulation becomes insufficiently resistive to prevent the formation of a gap-bridging channel and the consequent electrical breakdown of the insulation.

The metallization ion migration and dendrite growth follow paths of least thermodynamic resistance. Surface analysis (EDX) of exposed samples reveals that these paths often are surface paths, i.e., dissolved metallization ions have a tendency to proceed to the surfaces of the dielectric before undergoing interelectrode diffusion. Dendrites similarly grow back along the same least-resistance paths. These paths appear continuous to the eye, but electrical resistance measurements do not indicate electrical short circuits.

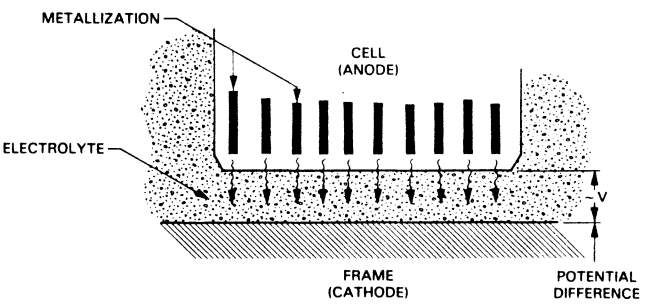

Fig. 2: The Electrochemical Degradation Mechanism

Definitions of Electrochemical Failure

The preceding discussion raises a question concerning the definition of a failure. It is thought that eventually a conductive path will short-circuit the anode-cathode (cell-frame) gap. This view evolved from the data in Fig. 3, first presented in [5]. The data are replotted here as the ratio of post- to pre-exposure cell power output versus quantity of interfacial charge transferred between anode and cathode per unit length of cell-frame edge. This latter quantity was calculated using measured encapsulant electrical conductivity values [5]. The cell power output remains fairly

steady until about 1 to 2 C/cm (charge per cm of edge length) has been transferred, after which the cell power output falls steeply to zero.

The data points near zero power output represent actual short-circuit failures, but sample damage was so severe that this failure condition cannot be attributed solely to the electrochemical degradation mechanism; for example, loss of plasticizer in the PVB due to test temperature in excess of 55°C resulted in embrittled encapsulant, and encapsulant shrinkage resulted in delamination.

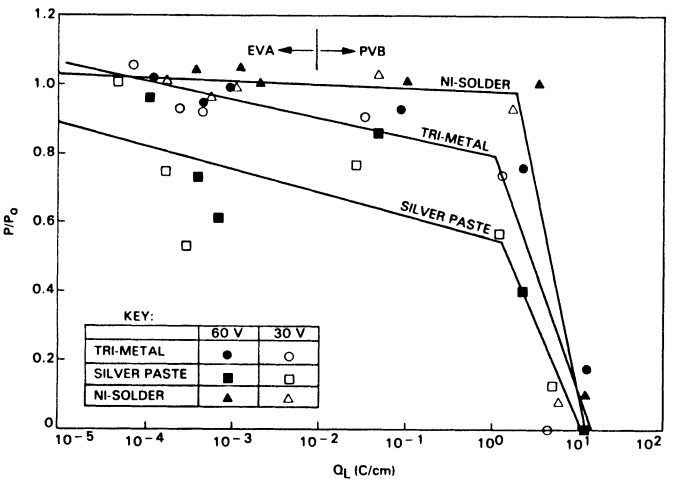

Fig. 3: Normalized Cell Power Output P/P_o versus Interfacial Charge Transfer per Unit Length Q_L (1944 hours of test exposure at 85°C and 0 to 100% relative humidity)

More carefully conducted charge transfer experiments, in which the charge transfer is measured directly (integrated leakage current measurements), have suggested failure criteria other than failure upon short circuit of the dielectric. One such criterion is failure when the cell leakage current (rate of charge transfer) exceeds a pre-specified threshold value. Another criterion focuses upon the device rather than the dielectric, i.e., failure when sufficient metallization has dissolved off of the silicon so that cell power output and its series resistance is severely compromised.

In the previous paper [5] the data of Fig. 3 were interpreted to imply that 50% cell failures occur upon passage between anode and cathode of about 0.4 C/cm. Such a criterion can be used to predict cell failure rates but is sensitive to the precise definition of failure assumed. It is clear that the concept of failure requires consideration of device performance as well as consideration of dielectric performance. Recent re-interpretation of the data in Fig. 3 suggests a better median cell failure criterion is 1 to 2 C/cm.

Accelerated Stress Testing

It is desirable to subject photovoltaic test specimens and modules to accelerated stress testing to determine, in a relatively short time, the expected life of modules to be deployed in a long-term field use environment. If the stress levels of the accelerated test do not excite degradation mechanisms other than those normally active at field stress levels, then one may cautiously presume that quantitative correlations between test time and field time are reasonably trustworthy.

Despite the lack of a precise definition of cell electrochemical failure, a quantitative correlation between chamber test time and field service time can be established. Assuming that equal amounts of charge transfer in the test and field environments result in equal amounts of degradation, it follows that [5]:

$$Y_{EQ} = \frac{Q_T}{\dot{Q}_F} = \frac{V_T}{V_F} \cdot \frac{K_T \tau_T}{\sum_i K_i \tau_i} \qquad (1)$$

where Y_{EQ} = years at field conditions equivalent to τ_T hours at test conditions, yr; Q_T = total charge transferred under test conditions, C; $\dot{Q}_F$ = total yearly charge transfer under field conditions, C/yr; V_T, V_F = test and field voltages, V; K_T = electrical conductivity of the encapsulation at the test T/H environment, $\Omega^{-1}m^{-1}$; τ_T = test time, h; K_i = electrical conductivity of the encapsulant of the field module when the cell temperature is T_i and the module internal relative humidity is H_i [3], $\Omega^{-1}m^{-1}$; and τ_i = number of hours per year that the field module experiences a cell temperature T_i and an internal relative humidity H_i, obtained from analysis of SOLMET weather data [5], h/yr.

The temperature- and humidity-dependent PVB and EVA electrical conductivities (K_T and K_i) are computed from formulas obtained by a global least-squares fitting of a family of polynomial equations to experimentally obtained data [5], as plotted in Fig. 4. It is immediately seen that typical module insulation electrical conductivities - and hence electrochemical degradation - increase as the encapsulant temperature and humidity increase.

The quantities $\sum_i K_i \tau_i$ for the several sites and encapsulants are presented in Table 1 for two scenarios: response to temperature stress only, and response to the multiple stresses of temperature and humidity. The temperature-only conditions are applicable to modules that have negligible humidity variation due to the use of moisture barriers such as metallic foils. The temperature-plus-humidity values, on the other hand, assume instantaneous equilibrium between the partial pressure of water internal to the module at its actual operating temperature and that in the ambient.

If field and test voltages are equal, then Eq. (1) is solved for τ_T, chamber test time equivalent to Y_{EQ} field years for the same electrode/electrolyte configuration, Figs. 5 and 6. Using these plots, chamber test conditions and test hours can be determined for PVB- and EVA-encapsulated modules, respectively, equivalent to 30 years of field exposure at sites ranging in diversity from Miami to Boston.

At high T/H combinations, less time is required to test PVB than EVA. This results from the significantly greater sensitivity of the electrical conductivity of PVB to relative humidity. This in turn is due to the unusually large ionizable species content of that encapsulant [6], perhaps associated with the added plasticizer, an additive lacking in EVA.

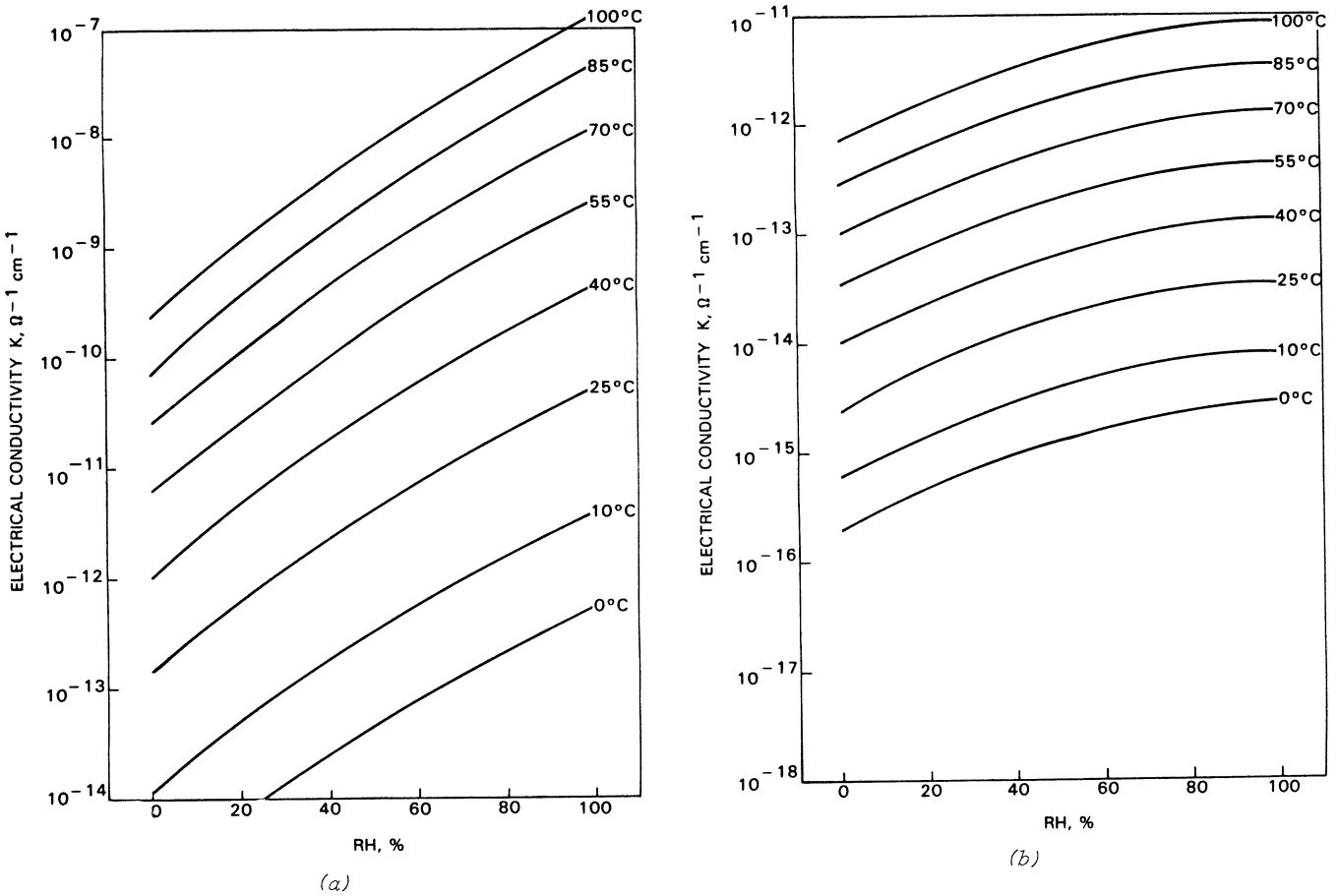

Fig. 4: Electrical Conductivity of PVB and EVA from 0 to 100°C and 0 to 100% Relative Humidity

Table 1

The Quantity $\sum_i K_i \tau_i$ at Selected Sites

	$\sum_i K_i \tau_i$, Ω^{-1} m^{-1} h/yr			
	Temperature Acceleration		Temperature and Humidity Acceleration	
Site	PVB	EVA	PVB	EVA
Albuquerque	1.12×10^{-6}	6.27×10^{-9}	1.89×10^{-6}	8.78×10^{-9}
Boston	2.96×10^{-7}	2.24×10^{-9}	1.26×10^{-6}	5.11×10^{-9}
Miami	9.11×10^{-7}	5.88×10^{-9}	5.72×10^{-6}	1.66×10^{-8}

Eq. (1) can be applied to the data of Fig. 3 to ascertain equivalent field time at, say, Miami, our "worst-case" site. The data points near zero cell power output correspond to 165 yr at 500 V in Miami. The points near the knees of the curves correspond to 40 yr, and the data points just to the right and left of the short vertical line segment correspond to 4 yr at 500 V in Miami.

Eq. (1) establishes an equivalence between field service time and accelerated-stress-test time based upon the concept that equal charge transfer in the two environments results in equal electrochemical damage. As such, it is useful in quantifying accelerated life testing for electrochemical solar cell degradation. This has been demonstrated above and will be demonstrated again below when interpreting results from a series of accelerated life tests on photovoltaic laboratory specimens and minimodules. Minimodules are specially manufactured test modules having smaller peripheral dimensions, and hence containing fewer cells than their commercial counterparts.

Module Qualification Test

The quantitative equivalence, Eq. (1), is also useful in interpreting the results of a qualification test ("qual" test). A qual test is a standardized series of tests (obstacle course) generally involving satisfaction of generic environmental stresses and pass-fail criteria that have little quantitative relationship to module-specific acceleration factors; hence, extracting quantitative information about electrochemical degradation from the results of a qual test is chancy.

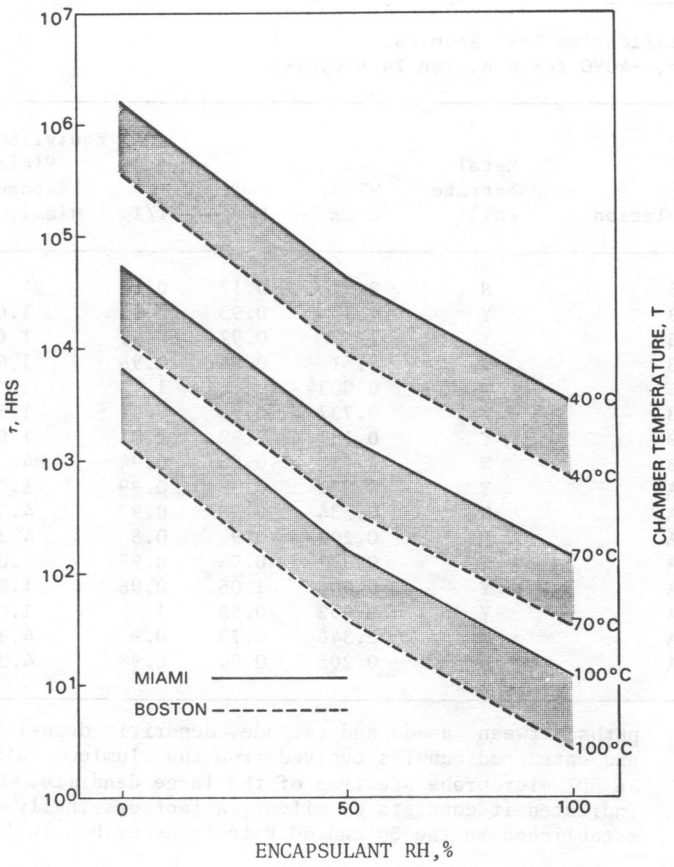

Fig. 5: Test time τ equivalent to 30 years field exposure for PVB-encapsulated electrodes

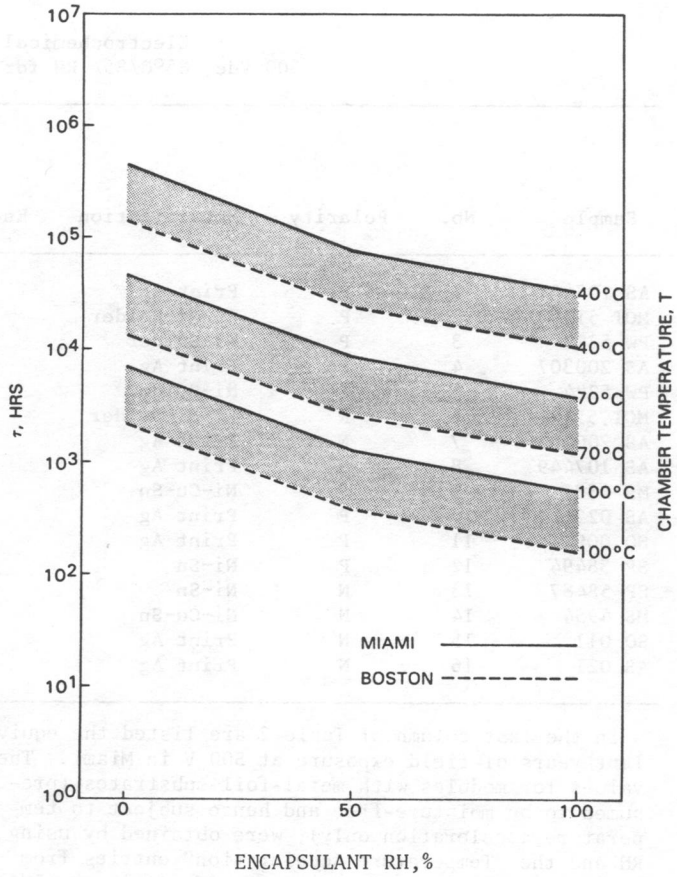

Fig. 6: Test time τ equivalent to 30 years field exposure for EVA-encapsulated electrodes

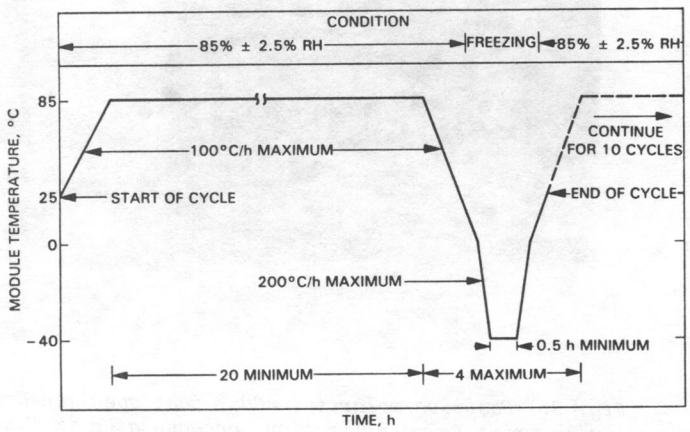

Fig. 7: JPL humidity-freezing cycle test

In the JPL Block V test sequence for photovoltaic modules [7], the test likely to offer the most electrochemical information is the "humidity-freeze" test. It consists of ten 24 h cycles: 20 h at a steady 85°C/85% RH, followed by 4 h during which the temperature is dropped to -40°C and then returned to 85°C, Fig. 7.

To examine the possible use of the Block V humidity-freeze test as a means of evaluating module sensitivity to electrochemical damage, sixteen minimodules were tested, two each of eight different design types, eight featuring PVB encapsulation and eight featuring EVA. All were stressed at 500 V between the shorted cell string and the frame; however, one module of each type was biased with cell string positive with respect to the frame (+ polarity) and the other module with cell string negative with respect to the frame (- polarity). The leakage current from each module was monitored every half-hour.

Interpretation of qual test results from an electrochemical damage point of view is complicated by the fact that test conditions were not steady; however, since metered charge transfer dropped to zero during the freeze phase of each cycle, the humidity-freeze test can be regarded as a 200 h accelerated stress at a steady 85°C/85% RH environment.

Some conclusions from the test results may be seen in Table 2. The charge transfer values per unit length of cell-frame edge, accumulated in 200 h of 85°C/85% RH exposure, are listed in the Q_{200}-column of Table 2. Generally, these values are largest for PVB modules and smallest for EVA modules. Use of a layered polymer/metal-foil film, such as Tedlar/Aluminum/Tedlar, as the module substrate, is effective in reducing leakage charge transfer, or leakage current, values in both PVB-encapsulated and EVA-encapsulated modules.

Table 2

Electrochemical Qualification Test Results:
500 Vdc, 85°C/85% RH for 20 h, -40°C for 4 h, Ten 24 h Cycles

Sample	No.	Polarity	Metallization	Encapsulation	Metal Substrate Foil?	Q_{200}, C/cm	P/P_o	I/I_o	Equiv. 500-V Field Exposure Miami, yr
AS 107461	1	P	Print Ag	PVB	N	2.91	0.17	0.32	84
MOT 5107	2	P	Pd/Ni-Solder	PVB	Y	1.17	0.95	0.91	1.6
PW 5222	3	P	Ni-Solder	PVB	Y	1.53	0.97	0.97	1.6
AS 200307	4	P	Print Ag	PVB	Y	3.61	0.96	0.96	1.6
PW 5224	5	N	Ni-Solder	PVB	Y	0.0034	1	1	1.6
MOT 5117	6	N	Pd/Ni-Solder	PVB	Y	0.737	0.79	0.97	1.6
AS 200303	7	N	Print Ag	PVB	Y	0.181	0.99	1.01	1.6
AS 107449	8	N	Print Ag	PVB	N	1.41	0.88	0.94	84
MS 4887	9	P	Ni-Cu-Sn	EVA	Y	0.031	0.98	0.99	1.0
AS 022	10	P	Print Ag	EVA	N	0.534	0.96	0.97	4.3
SO 009	11	P	Print Ag	EVA	N	0.202	0.9	0.8	4.3
SP 58494	12	P	Ni-Sn	EVA	Y	0.072	0.93	0.98	1.0
SP 58487	13	N	Ni-Sn	EVA	Y	0.006	1.06	0.98	1.0
MS 4954	14	N	Ni-Cu-Sn	EVA	Y	0.052	0.53	1	1.0
SO 011	15	N	Print Ag	EVA	N	0.346	0.73	0.9	4.3
AS 021	16	N	Print Ag	EVA	N	0.205	0.94	0.98	4.3

In the last column of Table 2 are listed the equivalent years of field exposure at 500 V in Miami. The values for modules with metal-foil substrates (presumed to be moisture-free and hence subject to temperature acceleration only), were obtained by using 0% RH and the "Temperature Acceleration" entries from Table 1 in Eq. (1). Values range from 1.0 yr (EVA) to 1.6 yr (PVB). Modules without a foil-back substrate are subject to temperature and humidity acceleration; using the appropriate entries from Table 1 in Eq. (1) gives values ranging from $4^{1/3}$ yr (EVA) to 84 yr (PVB).

In summary, adding voltage to the JPL Block V humidity-freeze test provides a qual test for electrochemical degradation of photovoltaic modules equivalent to 1 to 2 yr for foil-back modules and 4 to 85 yr for non-foil-back modules. These values vary proportionally with the test-to-field voltage ratio for example, a module that qualifies at 500 V for 4 yr also qualifies for 20 yr field service at 100 V.

The post- to pre-test maximum power ratio (P/P_o) and short-circuit current ratio (I/I_o) also listed in Table 2, do not exhibit a strong correlation with other parameters listed in the Table. Because of large power reductions, Modules No. 1, 6, 8, 14, and 15 failed the qual test. The major cause of power output reduction is attributed to short-circuit current losses resulting from optical obscuration and series resistance increases.

Two-Polarity Experiment

In this experiment two similarly constructed samples were tested at 500 V in a 70°C/98% RH environment. Sample construction consisted of a printed Ag cell and an aluminum bar (simulating a module frame) encapsulated in PVB. One sample was tested in positive polarity (cell +, aluminum -), the other in the opposite polarity. Figs. 8 and 9 show visual degradation after 99 test hours, equivalent to 15 years at Miami at the same voltage. Fig. 8 shows the positive polarity sample exhibiting the familiar electrochemical degradation pattern of dissolved metallization, diffusion paths between anode and cathode, dendritic deposits, and entrapped bubbles evolved from the aluminum cathode. An EDX microprobe spectrum of the large dendrite, Fig.8, indicated it consists of silver, a fact originally established in the 30 and 60 V tests described in [5].

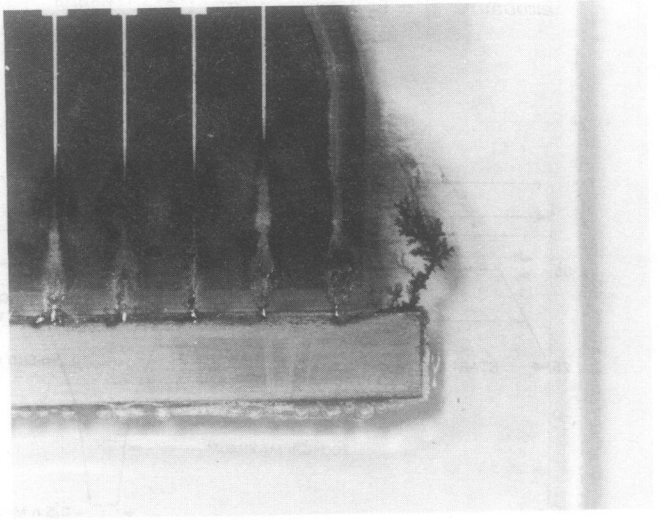

Fig. 8: Positive polarity, 500 V test specimen-Cell with print Ag metallization, encapsulated in PVB 70°C/98% RH, 99 test hours

The negative polarity sample, Fig. 9, shows none of these effects, but rather extensive cell (cathode) surface discoloration. Careful analysis indicated that this discoloration was actually delamination caused by cathodic gas evolution. The gas evolution was determined to have occurred at the metallization-silicon interface - the metallization has actually delaminated from the cell!

Other pertinent data were obtained. The insulation resistance of both samples dropped from about 1000 MΩ to about 2.5 MΩ. Measured unit charge transfers were 3.9 C/cm for the positive polarity sample and 3.2 C/cm for the negative polarity sample. From *I-V* curve data, Fig. 10, at the end of the test, power was down 30% in the positive polarity sample and 54% in the negative polarity sample. More extensive tests indicate that, although the degradation mechanisms in the two polarities differ, their rates are comparable. These results are important in considering degradation in center-tapped arrays wherein modules will experience both polarities of voltage stress, but at half the voltage differential to ground than would otherwise be the case in grounded single-polarity arrays.

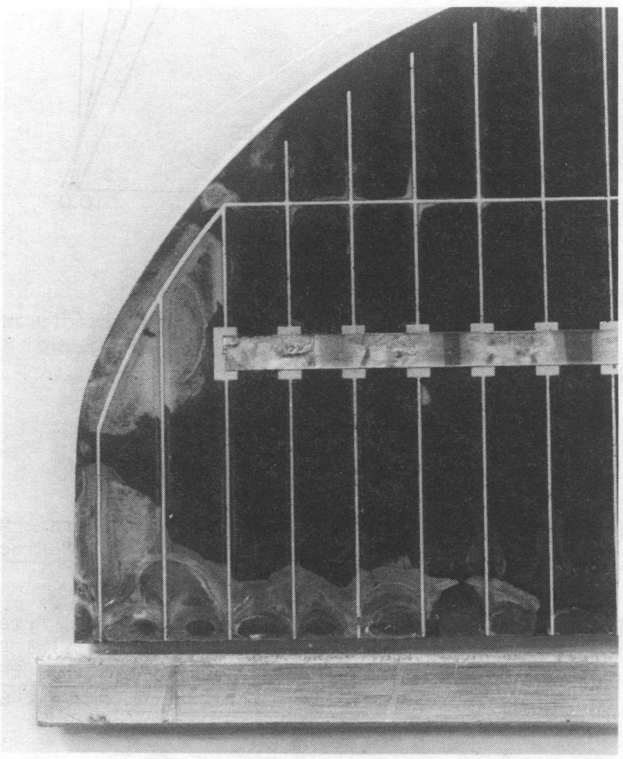

Fig. 9: Negative polarity, 500 V test specimen-Cell with print Ag metallization encapsulated in PVB, 70°C/98% RH, 99 test hours

CONCLUDING REMARKS

A causal relationship between photovoltaic device leakage current (quantity of transferred charge) and electrochemical damage has been qualitatively established.

Although a precise definition of device electrochemical failure is lacking, there is no evidence at this time to suggest that the fitted curves of Fig. 3 should not be used, as has been done previously [5], to define a median cell-failure level per unit length of cell-frame edge. The cell power degradation vs. charge transfer data from experiments discussed in this paper are plotted in Fig. 11 together with the best-fit straight lines from the previous low-voltage tests [5], Fig. 3. These data more or less support the conclusions drawn from those previous tests.

A quantitative relationship has been developed between chamber test time and field service time, based upon the supposition that equal quantities of charge transfer cause equal quantities of damage. This correspondence is given by Eq. (1). Although not quite a life prediction equation, it does give the interpreter of accelerated test data a feel for what can be expected of the test device in the real world, at least as pertains to electrochemical degradation of terrestrial photovoltaic devices.

It will be noted, from the above discussion of qual test acceleration factors, that temperature acceleration factors are similar for a large variety of module materials and constructions, but that humidity acceleration factors exhibit considerable variation. Use of metallized-foil substrate films will reduce this variation to levels comparable to those exhibited in modules experiencing temperature acceleration only.

An important result from the two-polarity test data is that the charge transfers for median cell failure in the two polarities are of the same order of magnitude, as are the corresponding degradation rates. This implies that center-tapped grounded photovoltaic arrays are a preferred system configuration to minimize electrochemical degradation, for maximum system voltage is half that which it would otherwise be in a grounded single-polarity array.

Finally, the role of the dielectric in solar-cell electrochemical degradation has been clarified: The greater the ion mobility in a particular encapsulant, the greater the cell-to-frame charge transfer, and hence the greater the electrochemical degradation. This is in accord with the findings of the coatings industry [8].

A good dielectric from the viewpoint of photovoltaic device electrochemical degradation is one that absorbs little water - even at elevated temperature/humidity combinations - or exhibits a low ionic concentration and mobility in the presence of water.

Since the presence of water may affect profoundly the electrical conductivity of photovoltaic device encapsulations, the investigation of water-dielectric interactions is of paramount importance to an expanded understanding of encapsulated photovoltaic device electrochemical degradation.

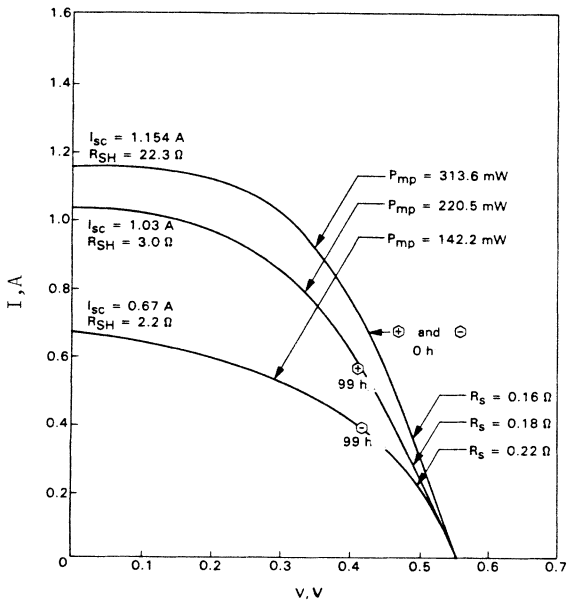

Fig. 10: I-V curve data for two-polarity experiment

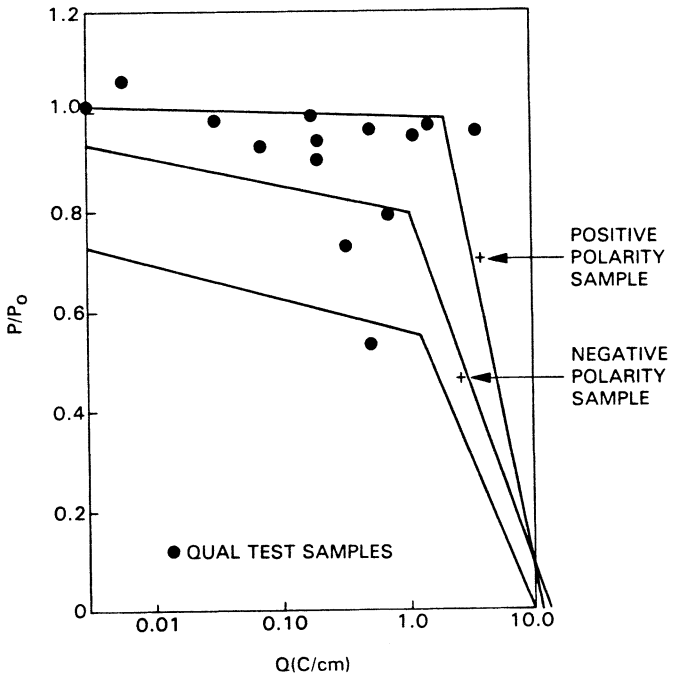

Fig. 11: Pre- to post-exposure power ratio versus unit charge transfer between cell and frame

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