

ELECTROCHEMICAL DEGRADATION OF AMORPHOUS-SILICON PHOTOVOLTAIC MODULES*

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ABSTRACT

Techniques of module electrochemical corrosion research, developed during reliability studies of crystalline-silicon modules (C-Si), have been applied to this new investigation into amorphous-silicon (α -Si) module reliability. Amorphous-Si cells, encapsulated in the polymers polyvinyl butyral (PVB) and ethylene vinyl acetate (EVA), were exposed for more than 1200 hours in a controlled 85°C/85% RH environment, with a constant 500 volts applied between the cells and an aluminum frame. Plotting power output reduction versus charge transferred reveals that about 50% α -Si cell failures can be expected with the passage of 0.1 to 1.0 coulomb/cm of cell-frame edge length; this threshold is somewhat less than that determined for C-Si modules. Both visual and electrical data reveal many of the same degradation phenomena observed in C-Si studies. Patterns of degradation apparently unique to α -Si have also been observed. Among the latter are pinhole-like loss of silicon material and stress corrosion of the aluminum metallization layer.

BACKGROUND

One function of a module encapsulant is to confine the generated electrical energy to the module circuitry. That energy which dissipates from the module circuitry through the encapsulant to nearby grounds (intentional or otherwise) is appropriately called leakage current.

If this dissipation is instantaneous, the encapsulant will have been electrically punctured. This catastrophic condition, characterized by an array short circuiting to ground, is called module breakdown or, more generally, voltage breakdown of the module's insulation.

If leakage current levels in a photovoltaic array are excessive, ground fault detection and protection equipment may be triggered (1).

When the leakage current has a fixed DC polarity, as is the case with photovoltaic modules, even levels of leakage current well below the ground-fault detection threshold are harmful, and are responsible for a form of long-term module degradation called electrochemical corrosion.

The fundamental principles of photovoltaic module electrochemical corrosion can be understood with the aid of Figure 1. Leakage current is composed of charge carriers that move under the influence of voltage and concentration gradients through the insulation, reacting with it and the cell and frame metals to produce corrosion products. Leakage current levels are determined in large part by the electrical conductivity of the insulation. This conductivity varies greatly with changing environmental conditions of temperature and relative humidity as indicated for

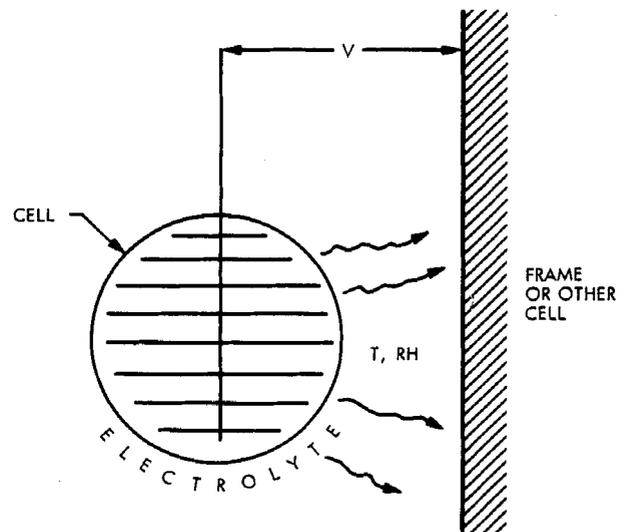


Figure 1. Corrosion Mechanism Overview

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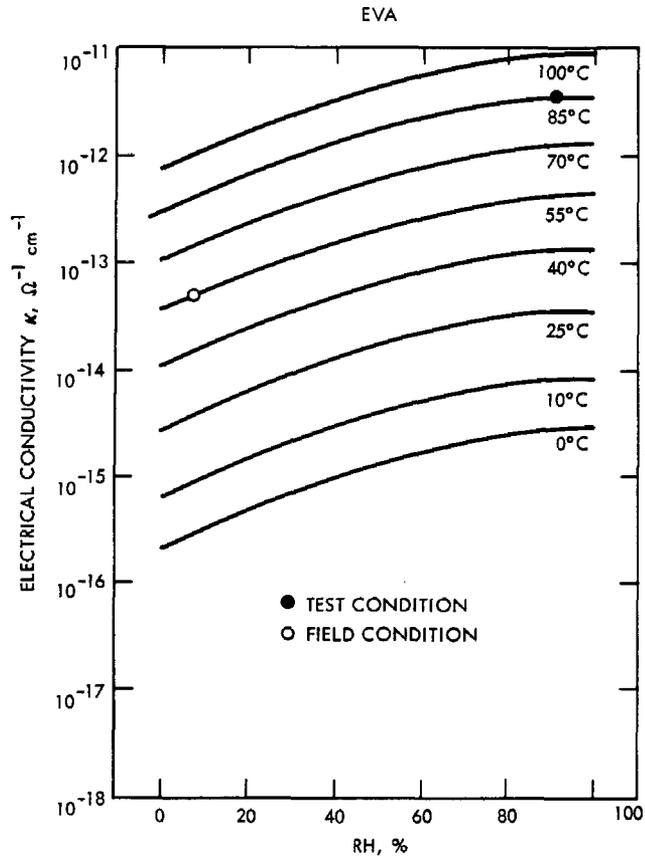
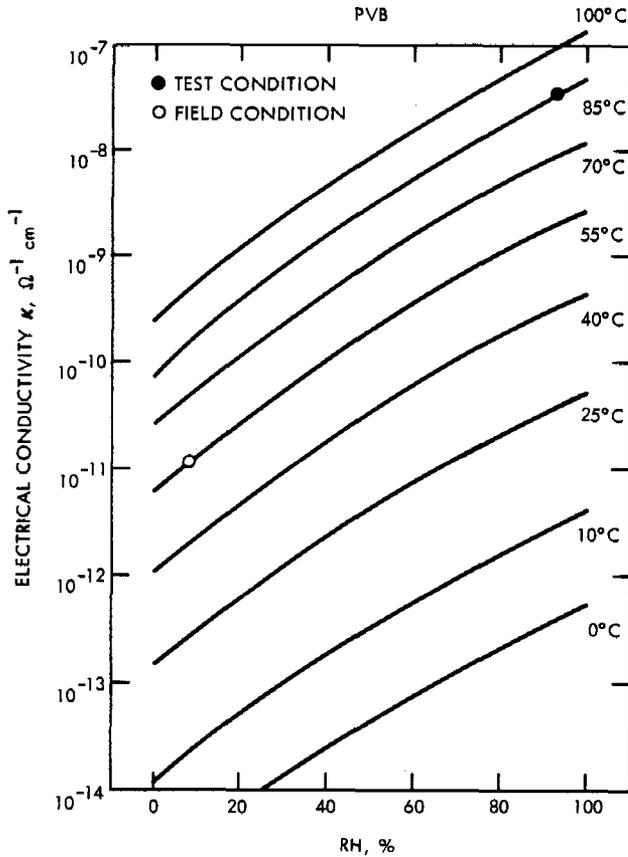


Figure 2. Bulk Electrical Conductivity of PVB and EVA

two popular photovoltaic insulation materials, polyvinyl butyral (PVB) and ethylene vinyl acetate (EVA), in Figure 2. Because of this high sensitivity to temperature and relative humidity, a typical 85°C/85% RH test environment, as used in this study, may have an acceleration factor of two to three orders of magnitude compared with field operating conditions. Also note that, for the same conditions of temperature and humidity, the conductivity of PVB is about three orders of magnitude greater than that of EVA.

Leakage current integrated over time yields the charge transferred between the cell and the frame. The quantity of charge transferred is an important measure of the total degree of electrochemical corrosion and resulting damage, such as cell power output reduction. Figure 3 quantifies this relationship between total charge transferred and reduction of cell maximum power output for crystalline-silicon (C-Si) modules. As shown, 1 to 10 coulomb/cm of charge transferred between cell and frame are required to produce a significant level (approximately 50%) of cell failures. The assumption that equal quantities of charge transferred in laboratory and field environments produce equivalent electrochemical damage, and the use of reduced SOLMET weather data, enables the determination of equivalent laboratory and field exposure times (2).

Typical corrosion observed in C-Si modules is depicted in Figure 4. With positive polarity

(cell positive relative to the frame), corrosion is characterized by loss of cell metallization and the formation of cathodic dendrites. The dissolved cell metallization ions have migrated to the frame, upon which they have deposited as dendritic crystallites. Typical corrosion in negative polarity exhibits less obvious characteristics to the naked eye, but microscopic examination reveals the formation of anodic corrosion salts and the evolution of gas bubbles at the cell's metallization-silicon interface, resulting in metallization delamination. Although the corrosion mechanisms in the two polarities differ, the degradation rates are comparable (3).

AMORPHOUS-SILICON TEST PROGRAM

Because amorphous-silicon (a-Si) cells differ significantly from C-Si cells in the quantity and types of materials involved, a test program was conducted to assess the effects of electrochemical corrosion on early production a-Si cells. It was expected that the ultra-thin layers making up the cells would make them especially vulnerable to corrosion; thus, establishing a preliminary estimate of the charge transfer sensitivity was an important objective.

Amorphous-Si submodules containing sixteen and eight cells, respectively, were obtained from two leading manufacturers, referred to as A and B (Figure 5). In the 16-cell submodule, all the

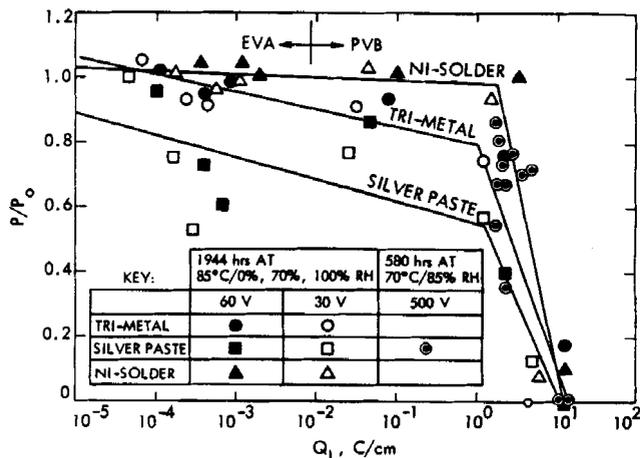


Figure 3. Power Output Reduction Versus Accumulated Unit Charge Transfer for C-Si Cells

cells are in parallel, sharing a common front electrode — the SnO₂ layer deposited on the underside of the glass superstrate. The eight-cell submodule consists of series-connected cells

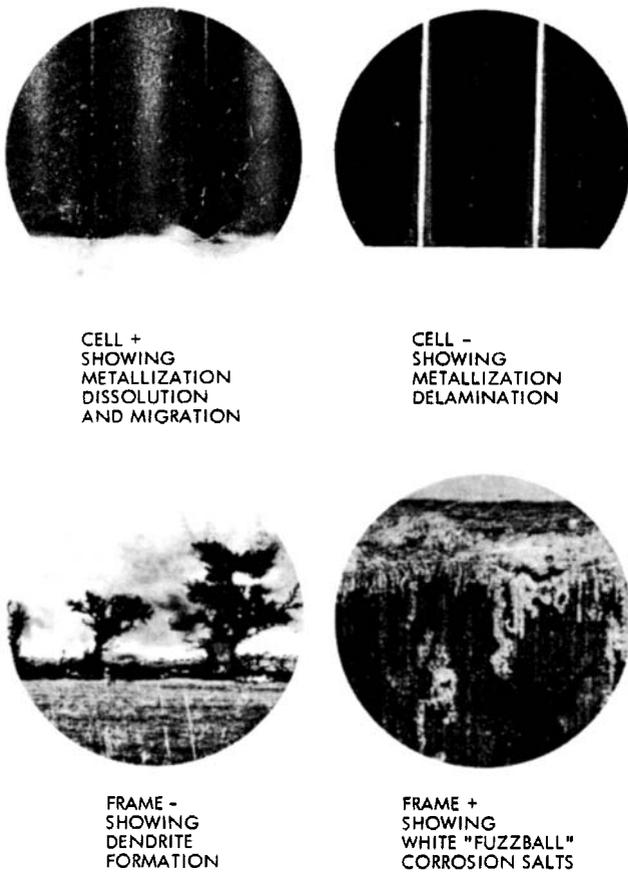


Figure 4. C-Si Cell Electrochemical Degradation in Two Polarities 500V, 580 h at 70°C/85% RH

with typical monolithically deposited overlapping interconnections.

To provide a controlled and known electrochemical environment, the submodules were each surrounded by a peripheral aluminum frame (Figure 5) to serve as the ground electrode, and the submodule-frame combinations were encapsulated in two well characterized encapsulants: PVB and EVA. Unprotected PVB, with its high conductivity, provides a highly accelerated corrosion environment and allows significant levels of charge transfer to be achieved in a rational test duration. EVA, with its high resistivity, more accurately reflects desirable field charge-transfer rates.

After encapsulation, all of the cells of each module were electrically shorted together with external jumper wires to become one electrode; the frame became the second. The specimens were then exposed, some for more than 1200 hours, in an environmental chamber at 85°C/85% RH, with 500 volts applied between cells and frame. Five modules from each of two manufacturers, A and B, were tested. Table 1 presents the individual module data including encapsulant, polarity of applied voltage, cell-frame gap spacing, and degradation observations. Automatic computer control of the test allowed the leakage current of each module to be monitored (Figure 6) and its integrated charge transfer to be continuously computed. Separate wires to the individual cells of each module also allowed cell I-V data to be acquired at periodic chamber down-times (Figure 7).

Overall Observations

Figure 8 displays the general loss of cell I-V performance versus charge transferred for the tested α -Si cells. When comparing this plot with the corresponding one for C-Si cells in Figure 3, one is led to the conclusion that α -Si cells are somewhat less rugged than C-Si cells with respect to electrochemical corrosion. Qualitatively, the level of sensitivity would seem to be entirely consistent with achieving excellent long-term corrosion life with a good high-resistivity corrosion-inhibiting encapsulant such as EVA.

The importance of minimizing total charge transfer is made clear by the extensive levels of degradation observed with the PVB-encapsulated modules as they neared 300 hours of exposure. With a test-to-field acceleration ratio of three orders of magnitude, this degradation would correlate to sixty-some years of field exposure. The exact acceleration ratio is sensitive to the details of module construction that influence encapsulant moisture level and surface resistivity. A dry, foil-protected PVB has a lower electrical conductivity, but also a much lower acceleration factor in the 85°C/85% RH test environment.

The differences between the two encapsulants are highlighted by the fact that, after more than 1200 hours exposure, only one of the EVA-encapsulated modules (Module 3) showed any appreciable degradation. This particular module was encapsulated as received from Manufacturer B who had supplied modules with a black protective coating that covered most of the submodule rear

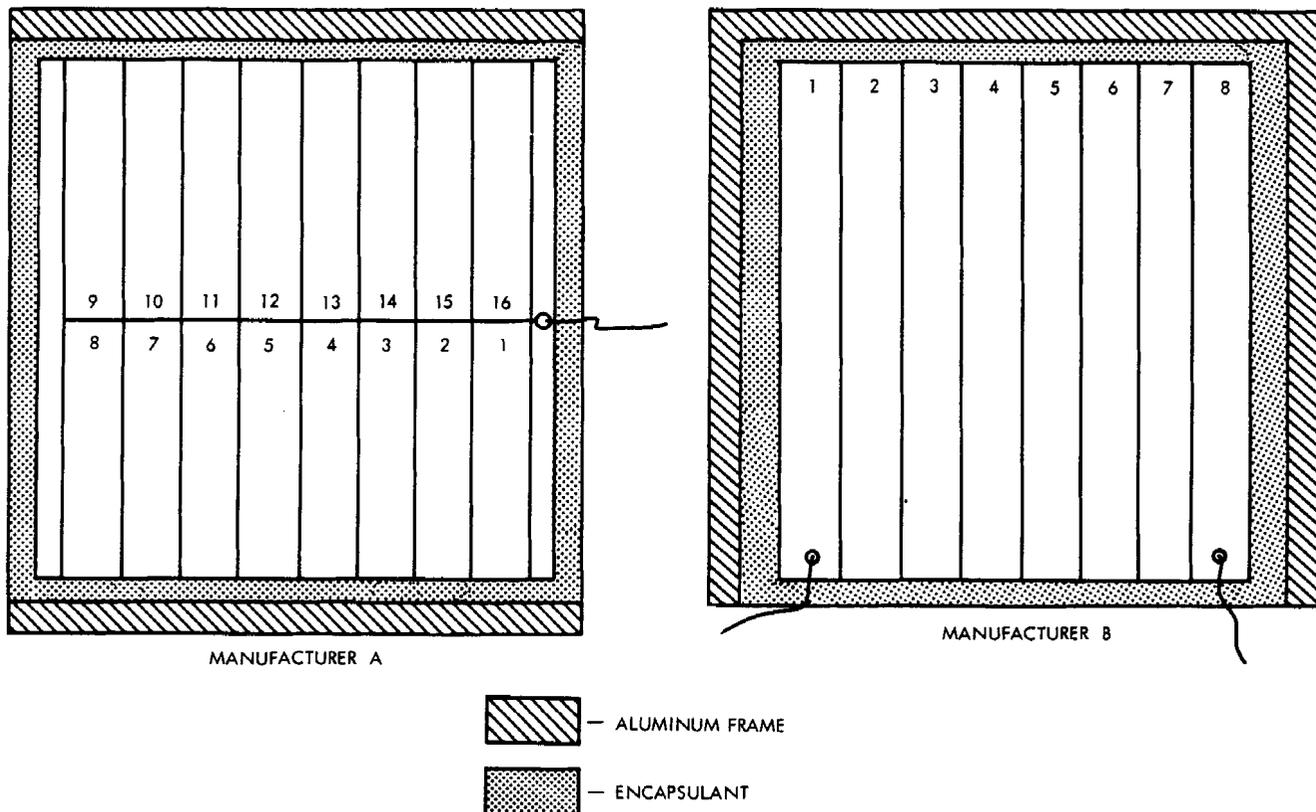


Figure 5. Amorphous Module Configurations

Table 1. Amorphous Module Test Parameters
(85°C/85% RH, 500 volts)

Module Manufacturer	ID	Encapsulant	Polarity (500 volts)	Electrode Gap (cm)	Test Exposure Time (h)	Damage
A	A688F	EVA	Positive	1.00	1250	Mild
	A694H	EVA	Positive	0.25	1250	None
	A686H	EVA	Negative	0.25	1250	None
	A666D	EVA	Negative	1.00	1250	None
	A690E	PVB	Positive	1.00	285	Severe
B	3	EVA	Negative	0.25	1250	Severe
	4	EVA	Positive	0.25	1250	None
	5	EVA	Positive	1.00	175*	Mild
	6	PVB	Negative	0.25	285	Severe
	7	PVB	Positive	0.25	285	Severe

* Module 5 showed no electrochemical degradation but was removed from the test early because the EVA melted and the module fell away from its frame, a consequence of faulty lamination.

surface. Prior to lamination, this coating was removed from the remaining modules from this manufacturer. At 40 hours, the uncoated metallization of Module 3 was observed to be

disappearing immediately adjacent to the black coating. By 130 hours, the visible metallization had totally disappeared. A post-test inspection (1250 hours) revealed that the aluminum had also

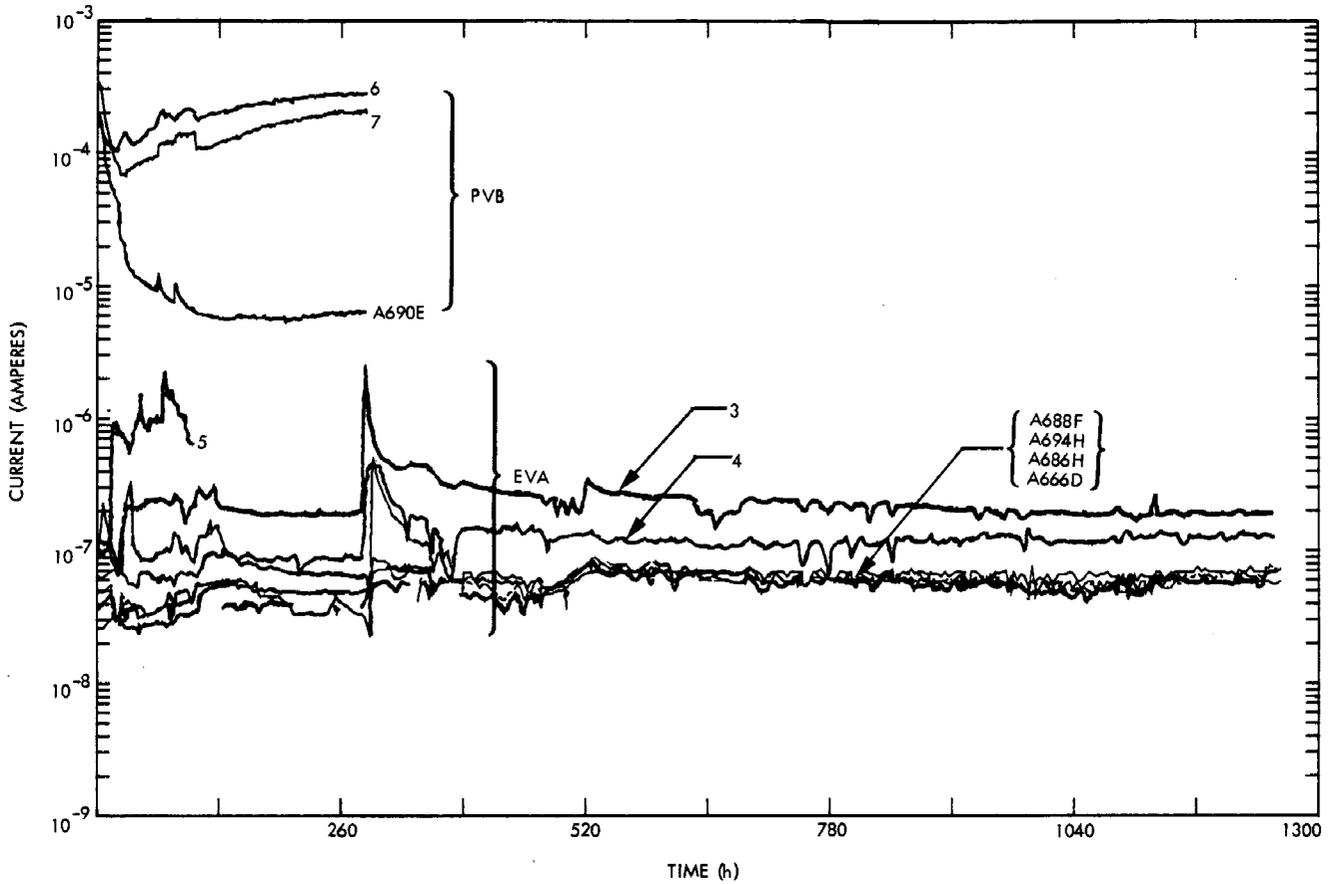


Figure 6. Amorphous Modules: Leakage current Versus Time of Exposure at 85°C/85% RH, 500 Volts

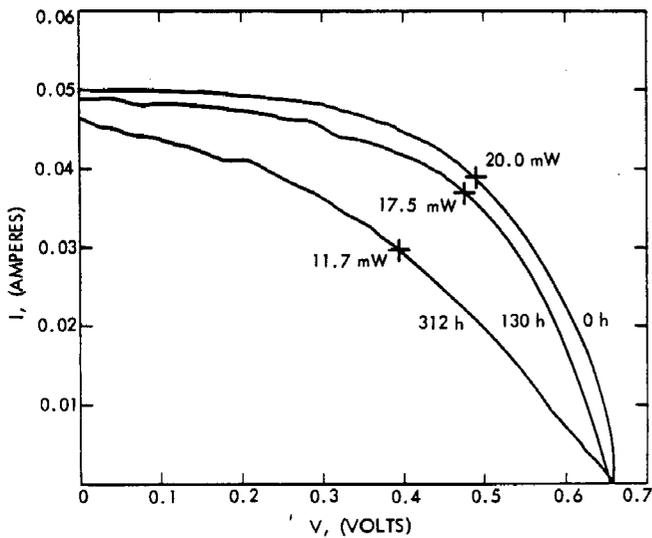


Figure 7. I-V Curves for Cell 6, Module A690E
85°C/85% RH, 500 volts

vanished from beneath the coating. Because this phenomenon was not observed on modules from which the coating had been removed, it is clear that the

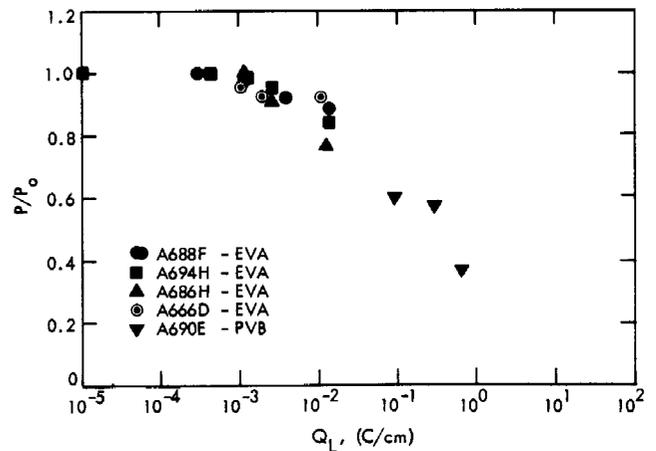


Figure 8. Power Output Reductions Versus Accumulated Unit Charge Transfer for Q-Si Cells

black coating severely compromised the corrosion inhibiting properties of the module.

Physical Analysis

The high-charge-transfer (PVB) samples suffered severe corrosion damage of a form not seen with C-Si cells.

Negative polarity (Module 6) resulted in a moving corrosion/diffusion front as evidenced by successive ridges in the encapsulation (Figure 9). These ridges were formed by swelling and setting of the encapsulation upon sample removal from the ovens at various down-times; they are indicative of ion movement toward or away from the positive frame electrode. Loss of metallization and amorphous silicon was pronounced. White corrosion salts were also observed on the frame (anode).

Positive polarity (Modules 7 and A690E) resulted in loss of aluminum cell metallization in squiggly, wormlike patterns (Figures 10 and 11). Electrode dissolution and ion diffusion are perhaps to be expected in this circumstance, but observation of these wormlike corrosion patterns is new.

To better understand the nature of α -Si module corrosion, several of the test samples were subjected to various surface and chemical analyses: A690E for Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectrometry (EDX) to determine the cause of the wormlike squiggly loss of aluminum metallization; A688F for SEM and EDX and Secondary Ion Mass Spectrometry (SIMS) to ascertain the cause of observed metallization discoloration; and Module 6 for SEM, EDX, SIMS, Fourier Transform Infra-red Spectroscopy (FTIR) and Ion Chromatography (IC) to reveal the nature of the anodic corrosion salts and to identify the species and direction of ion transport. The findings are as follows.

The metallization discoloration observed in EVA-encapsulated module A688F was revealed by SEM and EDX to consist of pellet-like entities, slightly smaller than one micron in diameter, attached to the aluminum metallization surface.

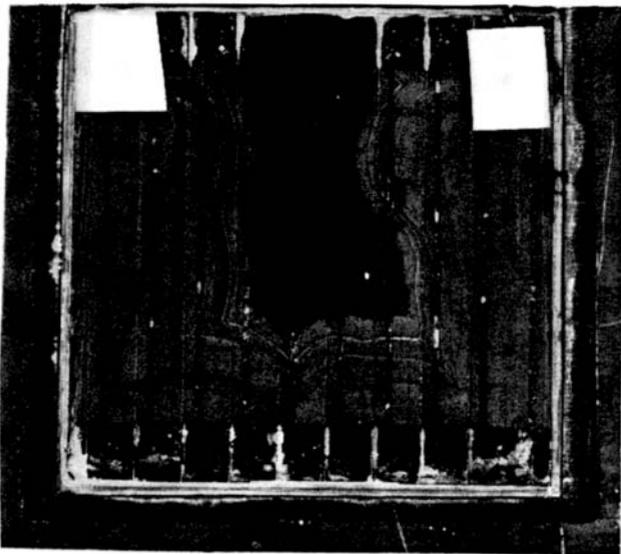


Figure 9. Corrosion/Diffusion Fronts - Module 6

SIMS revealed that these pellets consist of an aluminum oxide compound. The mechanism of their formation, however, is unknown at this time.

The cause of the wormlike loss of metallization observed on PVB-encapsulated modules (Figures 10 and 11) is more elusive. The conclusion drawn from surface analysis of these configurations is that the thin aluminum layer is undergoing stress corrosion. The SEM micrograph (Figure 12) reveals the unique propagation pattern in the aluminum layer.

The white salts on the aluminum frame (anode) of PVB-encapsulated Module 6 are also thought to be an aluminum oxide. FTIR analysis exhibits a transmission spectrum similar to that of oxidized aluminum alloy and rules out the possibility of aluminum hydroxide. Analysis by IC did not detect significant quantities of chloride, bromide, fluoride, nitrate, or sulphate ions in these salts. EDX, however, detected potassium and chlorine in the corroded regions behind the corrosion/diffusion front, but not in the uncorroded region ahead of the front (Figure 9). This suggests that aluminum ions, perhaps in the form of a negatively charged complex, are possibly migrating toward the frame and that chlorine-containing compounds are migrating away from the frame, or are at least actively participating in corrosion-forming reactions in the bulk PVB encapsulant.

DISCUSSION

Electrochemical studies of encapsulated α -Si and C-Si modules reveal a host of different damage mechanisms active in both module types. However, it is concluded that the governing corrosion mechanisms are similar — ionic interelectrode diffusion, with corrosion product formation at the ion/electrode interaction sites. Thus, the algorithmic machinery being developed to estimate useful C-Si module field lifetimes (2) and laboratory/field equivalent exposure times (3) should also be applicable to α -Si modules.

In a companion paper at this conference (4), it is pointed out that the minimum-resistance leakage current paths that control corrosion rate generally involve ion transport to and along material surfaces and intermaterial interfaces. In C-Si modules, where the cells are isolated from the environment by encapsulation on all sides, the corrosion rate is determined by the resistance of the encapsulant layer between the cell and the module rear surface. The rear surface, then, acts as a low resistance short to the module frame. The α -Si test specimens discussed here, and illustrated in Figure 5, have a similar encapsulant thickness isolating the submodule active surface from the frame member.

In contrast, typical commercial α -Si modules involving monolithic deposition on glass substrates, have no interface-free encapsulant isolating the cells from the module external surfaces. As shown in Figure 13, the cell-encapsulant interface provides an ionic conduction path directly to the module exterior, or to other cells of dissimilar voltage, in effect bypassing the encapsulant insulation. For such modules it would seem especially important to neutralize the ionic activity of this type of cell-encapsulant



Figure 10. Stress Corrosion in Module 7

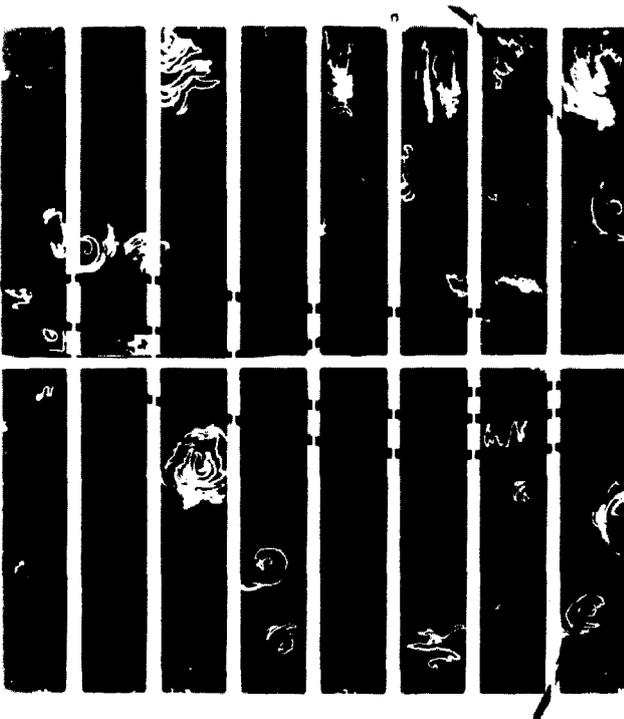


Figure 11. Stress Corrosion in Module A690E

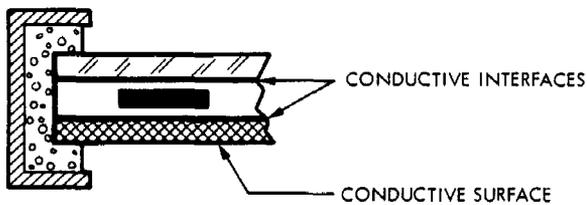
interfacial surface to the greatest extent practical. Achieving a strong interfacial bond through the use of properly selected primers is thought to be an important contributor to interface inactivity. The primer, and encapsulant itself, must also be made of high resistivity materials such as EVA.

As electrochemical corrosion results from ionic migration within and on the encapsulation, corrosion rates will be significantly lessened if ion-producing species and/or water, the ionizing agent, are kept away from the electrochemically active areas of a module. Barring water requires hermetic sealing; barring ion-producing species is achieved by avoiding contamination in the manufacturing process and by using module construction

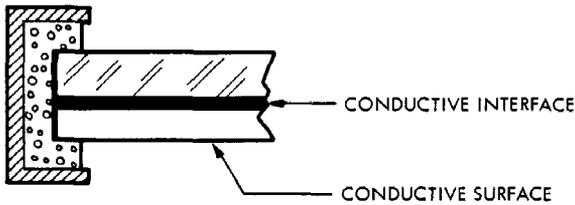


Figure 12. Wormlike Metallization Loss Pattern on Q-Si Module A690E, 40X

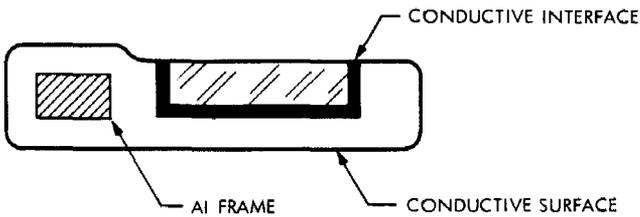
materials, especially encapsulants, with a low concentration of ion-producing species. PVB is known to have significant concentrations of ion-producing species, which accounts for its significantly higher conductivity compared to the virtually "non-ionic" EVA.



A) TYPICAL C-Si MODULE



B) TYPICAL α -Si MODULE



C) α -Si TEST SPECIMEN

Figure 13. Module Schematics

CONCLUSIONS

Based upon gathered module power output versus charge transfer data, it is concluded that encapsulated α -Si cell degradation rates are somewhat greater than those of C-Si cells exposed to similar electrochemically active environments. However, when a good, high-resistivity corrosion-inhibiting encapsulant such as EVA is used, α -Si modules should have excellent long-term corrosion durability. A complicating factor making it more difficult to insulate monolithic thin-film cells

is the common interfacial cell-encapsulant surface connecting all cells with the module exterior.

The greater corrosion sensitivity of these thin-film cells, and the presence of this bonded interface, demand that the encapsulation of α -Si modules be treated judiciously. Additional research is necessary to more thoroughly quantify thin-film-module encapsulation techniques, and is ongoing (4).

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REFERENCES

1. Levins, A., and Sugimura, R., "Photovoltaic Array Grounding and Electrical Safety," Progress in Solar Energy, AS-ISES, pp. 1061-1066, 1982.
2. Mon, G., Orehotsky, J., Ross, R. Jr., and Whitla, G., "Predicting Electrochemical Breakdown in Terrestrial Photovoltaic Modules," Proceedings of the 17th IEEE Photovoltaic Specialists Conference, pp. 682-692, 1984.
3. Mon, G., Whitla, G., Neff, M., and Ross, R. Jr., "The Role of Electrical Insulation in Electrochemical Degradation of Terrestrial Photovoltaic Modules," IEEE Transactions on Electrical Insulation," in press, 1985.
4. Mon, G., Wen, L., Ross, R., Jr., Adent, D., "Effects of Temperature and Moisture on Module Leakage Currents," Proceedings of the 18th IEEE Photovoltaic Specialists Conference, Las Vegas, Nevada, October 21-25, 1985.