ELECTROCHEMICAL AND GALVANIC CORROSION EFFECTS IN THIN-FILM PHOTOVOLTAIC MODULES *

G. Mon,[1] L. Wen,[1]
J. Meyer,[2] R. Ross Jr.[3]

Jet Propulsion Laboratory
California Institute of Tecnology
Pasadena, CA

A. Nelson,[4]

Solar Energy Research Institute
Golden, CO

ABSTRACT

In this paper the electrochemical and galvanic corrosion properties of thin-film photovoltaic (TF-PV) module and module sub-components are determined and interpreted in light of established corrosion science. Results of a detailed study of thin-film aluminum metallization corrosion are presented. "Bar-graph" corrosion, observed in fielded modules, has been experimentally induced and determined to be electrochemical in nature. Corrosion rates and passivation techniques for TF-PV modules are discussed.

INTRODUCTION

Electrochemical corrosion in PV modules is driven by applied or photovoltaically generated potential differences between conductor elements that are separated by an ionically conductive electrolyte, such as between cells and frame in both crystalline-silicon (C-Si) and amorphous-silicon (a-Si) modules. The interelectrode current is responsible for oxidation (dissolution) reactions at the anode and reduction (plating) reactions at the cathode. Two undesirable TF-PV module life-limiting conditions may result from cell-to-frame leakage currents: (1) dissolution of TF current-carrying elements, which can result in open-circuiting, and (2) the formation and migration of reaction product that can short-circuit the interelectrode (cell-to-frame) gap.

Galvanic corrosion occurs when two dissimilar material conductors contact each other in an electrolytic medium. No external or PV-generated potential differences are required. Hence galvanic corrosion can occur day and night. Examples in a-Si PV modules, Fig. 1, include corrosion along the zone of contact between the front surface transparent conductive oxide (TCO--usually SnO_2) and the back surface aluminum (Al) metallization, or between any bridging conductor material (such as Ag paste stitch lines) and either the TCO or the Al metallization. We shall also include as galvanic corrosion any observed corrosion that apparently involves only one conductor--for example, the corrosion of the Al metallization in the presence of oxygen and moisture, so-called differential aeration corrosion, Fig. 2.

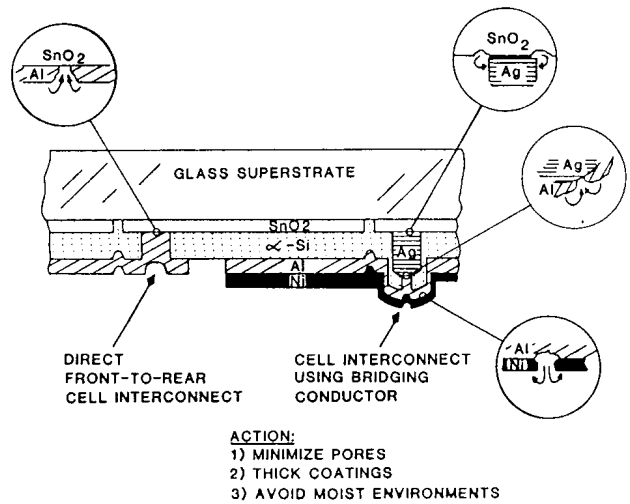

Fig. 1. Galvanic Current Flow at Defects in Thin-Film Photovoltaic Module Coatings

Corrosion Experiments

Several experiments were conducted to investigate the nature of chemical corrosion of TF-PV modules and module sub-components. The experiments were of two types: (1) chemical characterization, and (2) environmental exposure.

Chemical Characterization. By chemical characterization we mean that chemical I-V curves and Tafel curves were obtained for each sample acting first as an anode against an Al cathode, and then

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1 Member of the Technical Staff, Reliability Physics Subgroup, Applied Technologies Section, JPL.
2 Academic Part Time, Reliability Physics Subgroup, Applied Technologies Section, JPL.
3 Manager, Thin-film Module Reliability Research Task, Applied Technologies Section, JPL.
4 Surface and Interface Analysis Lab, SERI.

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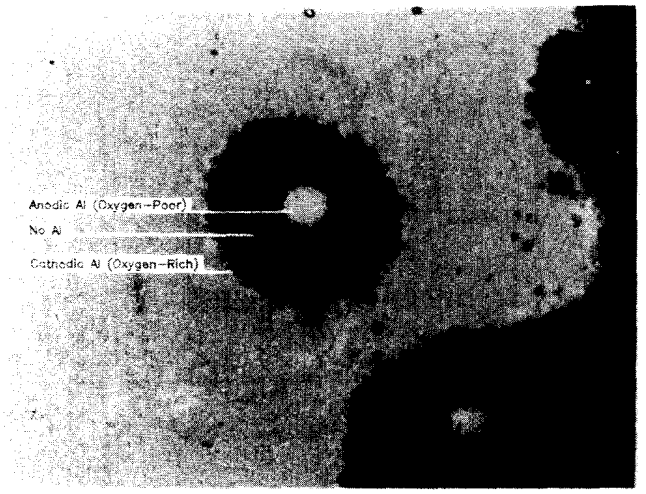


Fig. 2. Differential Aeration Corrosion of Thin-Film Aluminum on a Glass Substrate

as a cathode against an Al anode in pH = 3 HCl or other appropriate electrolyte. A chemical I-V curve is a device I-V curve with the anode-electrolyte-cathode serving as the "device". From such data, electrolyte and/or electrode encapsulant resistivity can be determined.

For a single electrode, Tafel curves are plots of electrode overpotential (i.e., polarization), as determined by a standard calomel reference electrode (SCE) vs polarization current or current density. The polarization current density i is proportional to the corrosion reaction rate and is derivable from physical considerations of the electrode/electrolyte interface together with kinetic considerations of molecular interactions [1] or, less generally, from thermodynamic considerations [2]. The overpotential n is essentially the potential difference between the electrode and the bulk electrolyte; in the parlance of the electrochemist, it is the voltage drop across the double-layer of a polarized electrode. The relation between these quantities is $n = B*\log(i/i_0)$, where B is a constant and i_0 is the equilibrium or exchange current density.

Environmental Exposure. Environmental exposure tests, usually accelerated, are conducted for the purposes of observing corrosion phenomena and of determining corrosion rates. Such tests may include exposure to corrosive electrolytes or to controlled temperature/humidity environments with monitoring, either in situ or during periodic down times, of some appropriate index of changing sample conditions, such as charge transfer rate or surface resistivity.

ELECTROCHEMICAL CORROSION

Polarization

When current flows to or from an electrode, there may be a noticeable change in the electrode-to-electrolyte potential. If so, the electrode is said to be polarized.

The polarization of various module elements serving as electrodes vs a reference SCE electrode in pH = 3 HCl has been measured. The results are shown in Fig. 3. It is evident from the depicted behavior

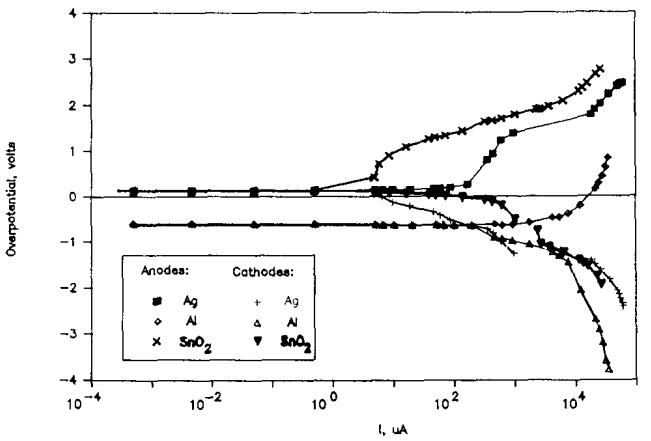


Fig. 3. Module Element Polarization Curves vs SCE in pH = 3 HCl

that there exists an activation energy of polarization and a corrosion potential for various anode-cathode combinations which establishes the corrosion rate for that system. For example, the cross-over point of the Al (anode) and TCO (cathode) curves establishes the corrosion potential for this system at about -0.5 volts; the corresponding current, about 1.5 mA, is the corrosion rate: it is the coulombs per second of charge transfer occurring at both electrodes. This rate can be converted into corresponding mass loss (anode) or plating (cathode) rates using Faraday's law [3]: $M = (W/zF)*\text{integral}\{I*dt\}$, where integral{I*dt} is the transferred charge responsible for the dissolution or deposition of M grams of a substance of atomic weight W and valency z, and the Faraday F = 96,500 Coulombs/gram-equivalent.

Al-Metallized Glass

Characterization. A major experimental study of TF-PV module back-surface Al metallization corrosion was undertaken in cooperation with several thin-film module manufacturers who supplied us with their commercial Al metallizations deposited on JPL-supplied Pyrex 7740 borosilicate glass and, in one case, additionally on the manufacturer's own chemically tempered soda-lime glass. Featured were vacuum-evaporated films, sputtered films, low and high purity films, and films with a nickel flash. At issue were whether variations in corrosion resistance derive from properties inherent in the films themselves or in the glass substrates, and the degree to which the encapsulant systems play a role in retarding or accelerating corrosion.

The various samples of different manufacture--encapsulated and not--were first chemically characterized in pH = 3 HCl and were then subjected to 1910 hours of exposure in an 85°C/85%RH environment with periodic down-times for surface resist-

ivity measurements.

During characterization, the interelectrode resistivity was first determined from I-V curve data, Fig. 4, using the equation $rho_v = E/j$, where rho_v (ohm-cm) is the bulk interelectrode resistivity (the slope of the curves in Fig. 4), E (volts/cm)

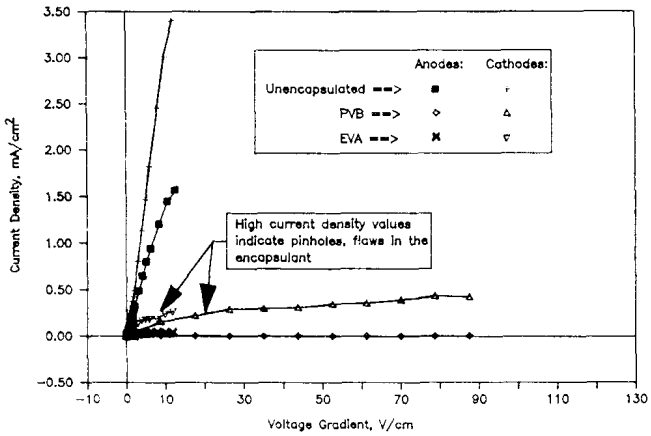


Fig. 4. Chemical IV Curve (Thin-Film Aluminum on Borosilicate on Glass

is the applied field, and j (amps/cm^2) is the current density determined at the sample; and then the resistance R (ohm) was determined from $R = rho_v*(l/A)$, where l (cm) is the interelectrode distance and A (cm^2) is the sample submersion area.

The electrolyte resistance measured to be about 500 ohms to 800 ohms. In general, the PVB- and EVA-encapsulated electrode resistances measured considerably less than expected from previously measured bulk resistivity values of these encapsulants [3]. An inspection of the sample encapsulations revealed microscopic delaminations and pinholes. These flaws were corrected before continuing.

After characterization, visual inspection revealed that encapsulated samples exhibited little loss of metallization. Unencapsulated samples serving as cathodes generally remained intact--they exhibited no Al loss--except for the low purity TF-Al on the chemically tempered glass. The TF-Al on unencapsulated anode samples completely dissolved.

The Tafel curves, Fig. 5, exhibit variations of overpotential with current density. Current density must increase considerably before large electrode polarizations are observed. Not unexpectedly, the characterizations of all of the unencapsulated samples are similar, as are those of all the encapsulated samples. A major observation is that the electrode polarizations are not necessarily symmetrical. Unencapsulated samples polarized cathodically. Encapsulated samples exhibited very large anodic polarizations, almost equal to the applied voltage (up to 500 volts), and very small cathodic polarizations. Another major observation is that, for the same degree of polarization (as measured by the overpotential), the corrosion current level, and hence corrosion rate, for encap-

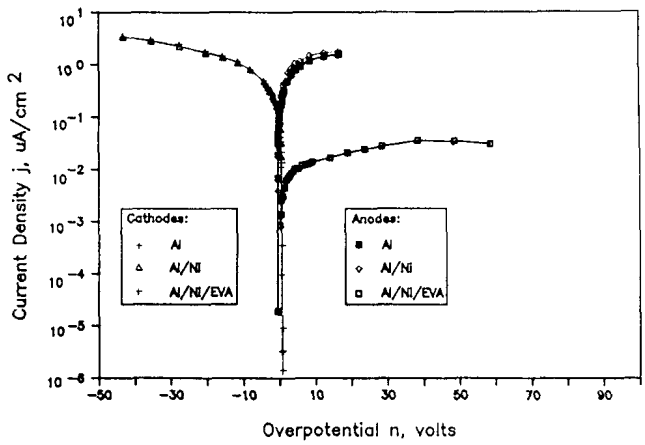


Fig. 5. Tafel Curves for Thin-Film Aluminum Metallization on Glass

sulated samples is lower by at least two orders-of-magnitude than for unencapsulated samples. Additional data and results of testing these manufacturer-supplied samples are presented later.

Dependence on pH. Tafel curves generated on encapsulated Al/glass samples in electrolytes ranging in pH from 3 - 11 exhibited little dependency on pH, Fig. 6. Uhlig [2] shows a flat minimum

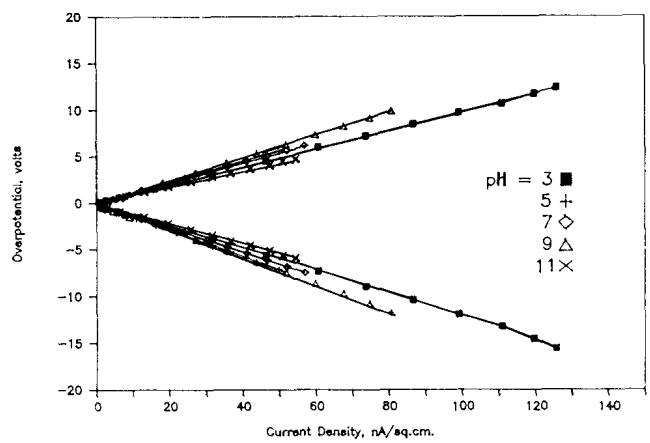


Fig. 6. Tafel Curves for PVB-Encapsulated Thin-Film Aluminum Electrodes as a Function of Electrolyte pH

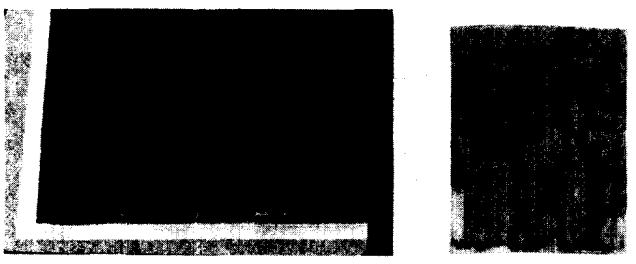
in the corrosion rate for commercially pure (CP) Al for 4 < pH < 7.

Passivation. It has already been shown that encapsulation considerably reduces metallization corrosion. Additional observations of interest during characterization were as follows. The nickel flash did not protect the TF-Al from the pH = 3 HCl environment and, in fact, increased the difficulty of encapsulating the metallization with EVA. Generally, evaporated films fared more poorly than sputtered films, and films on the chemically tempered glass dissolved more readily in an aqueous

electrolyte than did that same manufacturer's film deposited on the apparently more passive borosilicate glass surface.

Tests on Submodules

Glass/TCO Interface: Bar-Graph Corrosion. SEM/XPS analysis of manufacturer-supplied glass/TCO samples exposed to pH = 3 HCl with 60 volts and 200 volts bias revealed that cathodic samples corroded from the TCO surface, inwardly, converting transparent conductive SnO_2 to black, non-conductive SnO, which flaked off the glass ($e^- + SnO_2 + 4H \Longrightarrow SnO + H_2O + H_2\uparrow$). $Sn(OH)_4$, $Sn(OH)_2$, and Sn(OH)Cl were also formed. Sample anodes tended to delaminate at the glass/TCO interface due to chemical attack of the glass itself. This corrosion mechanism has actually been observed to occur in the fielded modules of at least two manufacturers and has been induced electrochemically in modules in our laboratory. It is called "bar graph corrosion" because individual (and not necessarily adjacent) cells of a module are attacked and removed from the substrate by this process, giving the appearance of a bar graph, Fig. 7.



Field Laboratory

Fig. 7. "Bar-Graph" Corrosion

Encapsulant Resistivity via Characterization. Characterization of these samples against Al electrodes in pH = 3 HCl, gave results similar to those obtained for Al metallization on glass. The resistivity of the electrode encapsulant, PVB in this case, was determined from these characterizations. Its resistivity, at 22°C/immersion, is determined from the tangent at the origin of the Tafel curve, plotted on linear scales in Fig. 8, to be 1000 M-ohm-cm. The bulk resistivity of EVA, measured as an electrode layer resistance, is 3500 M-ohm-cm. These measurements compare favorably with data previously obtained at 25°C/100%RH using concentric cylinder-and-guard-ring electrode techniques [3].

GALVANIC CORROSION

Galvanic Potential of Module Elements

Various conductive elements contact each other in a typical TF-PV module, resulting in "contact" potentials. In some modules the back surface metallization layer directly contacts the TCO layer, while in modules featuring a bridging conductor such as glass frit with Ag paste there are two sets of conductive contacts--the Al/Ag and the Ag/TCO

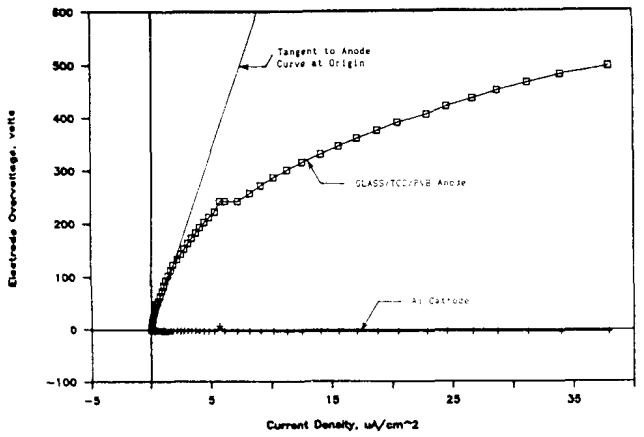


Fig. 8. Chemical Characterization Curve for GLASS/TCO/PVB vs Aluminum, SCE, in pH = 3 HCl

couples, Fig. 1.

The results of measuring these galvanic potentials, using manufacturer-supplied Ag/TCO/glass, TCO/glass, and Al/glass samples, are presented in Table 1.

Aluminum Metallization on Glass

We report here the results of exposing the manufacturer-supplied Al metallizations on glass to an 85°C/85%RH environment. The encapsulated samples corroded very little. The unencapsulated samples exhibited wide variation, ranging from almost no corrosion to highly mottled surfaces to almost complete loss of metallization. The nickel-flashed metallization tended to develop a dull surface appearance (fogging) shortly after exposure to the 85°C/85%RH environment, probably resulting from airborne sulphate contaminants [2]. This sample eventually developed extensive localized regions of metallization loss, whereas the unflashed metallization from the same manufacturer developed a mottled appearance but exhibited little loss of Al. The evaporated and sputtered films of a second manufacturer corroded, but not seriously; their surfaces exhibited blotches and pinholing, but the metallization remained essentially intact.

Apart from some pitting corrosion, the low-purity films of the third manufacturer proved to be tenaciously adherent to both the chemically tempered soda-lime and the borosilicate glass substrates, while the high-purity films of the same manufacturer adhered adequately to the borosilicate glass (with a mottled appearance) but almost completely disappeared from the chemically-tempered soda-lime glass, Fig. 9.

The generally observed signature of pitting corrosion in TF-Al metallization is a "bull's eye" pattern: an island of oxygen-poor (anode) original metallization surrounded by an Al-free moat, the outer boundary of which is oxygen-rich (cathode), Fig. 2; the bull's eye is, in fact, a differential aeration cell. This type of corrosion usually

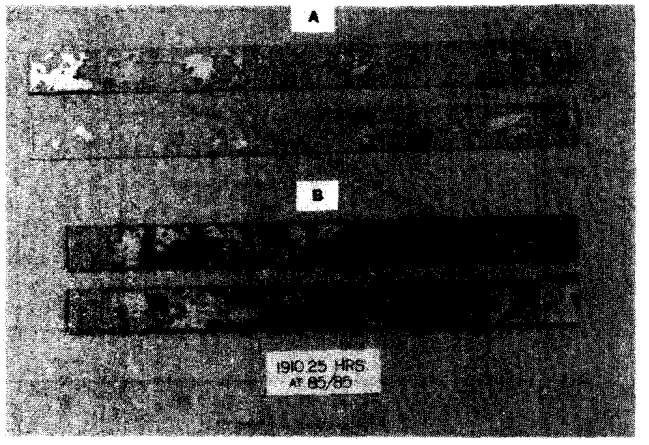


Fig. 9. Corrosion of Thin-Film Aluminum on (A) Chemically Tempered Soda-Lime Glass and (B) Borosilicate Glass after 1910 Hrs @ 85°C/85%RH

requires Cl ion [2] which is supplied by handling and airborne salts.

The periodic resistivity data was obtained out-of-oven using a Kelvin (four-point) probe technique. Unencapsulated samples exhibited metallization losses to varying degrees, but measurements were made on those portions of the metallization that were still intact. These readings showed surprising constancy over the 1910 hours of exposure time, Fig. 10. Unencapsulated specimens exhibit some

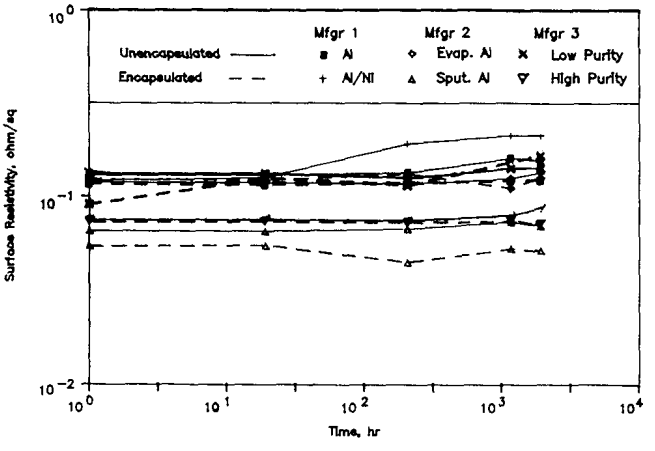


Fig. 10. Metallization Resistivity vs Exposure Time @ 85°C/85%RH

small, essentially insignificant increase in metallization resistivity with time of exposure compared to EVA-encapsulated samples. The sputtered film of Mfgr. 2 is less resistive than the evaporated film, just as the high-purity film of Mfgr. 3 is less resistive than the low purity film. In one case-the high-purity film on chemically-tempered glass-much of the metallization disappeared.

Whereas data from a similar study of metallization corrosion on fully metallized back surface modules [4] showed the encapsulation to be ineffective in retarding corrosion, the present data show the encapsulation to be marginally effective. The minor differences in measurement results may depend upon major differences in the samples: the previous samples were modules having not only interceding material layers between the Al metallization and the glass substrate but also intercell zones (scribe lines) which are suspected to be preferential avenues for moisture ingress into TF-PV modules [5].

DIRECT MEASUREMENT OF CORROSION RATE

The anodic loss rates in pH = 3 HCl of two manufacturer-supplied bare TF-Al metallizations was determined from Faraday's Law, M = (W/zF)*integral{I*dt}, by recording the time and current required to dissolve the immersed coating area. The results, normalized to 1 uA continuous current, are as follows: 4350 A/yr (Angstroms/yr) for the sputtered film of Mfgr. 2 and 3210 A/yr for the high-purity film of Mfgr. 3.

It may be possible to calculate the life of a fielded module from such results by summing metallization thickness losses based upon intelligent estimates of expected field leakage currents. For example, it is known that leakage currents are generally highest in the morning when the sun powers up dewy modules. Assuming a 10 uA leakage current level for 1 hour each morning, a 4000 A metallization will survive almost 3 years.

DISCUSSION

It was initially thought that the bar-graph corrosion first observed in one manufacturer's fielded modules resulted, not from contact with the electrolyte solution, as is now known, but from the fact that the superstrate glass was chemically tempered, hence possibly had a higher chemical activity or surface ion concentration. The surface conductivity of the tempered glass was measured and found to be actually lower than that of the non-tempered green glass usually employed as thin-film module superstrates.

Characterization testing, especially chemical I-V curve acquisition, may be a simple technique that module manufacturers can use as a production line electrochemical qualification test procedure--testing especially the quality of the insulation [6].

First observation of bubbles during characterization experiments occurs at current levels at which polarization is first activated. To prevent deleterious delaminations, corrosion currents should be maintained at a level low enough to allow the gaseous reaction product to diffuse away rather than accumulate at the electrode/encapsulant interface. Bubbles were first observed at about 25 uA/cm^2 for glass/TCO samples and at about 7 uA/cm^2 for glass/TCO/PVB samples.

An approach to reducing module corrosion currents other than passivation may be to provide an elec-

trically isolated sacrificial conductive layer surrounding the cell plane.

CONCLUDING REMARKS

It has been the purpose of this paper to consider TF-PV module corrosion against the backdrop of historical corrosion science. Such an approach holds promise of providing a quantitative basis for module design.

ACKNOWLEDGEMENTS

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Table 1

Mfgr	Polarity (+)	Polarity (-)	Voltage, mV Dry	Voltage, mV pH = 3 HCl	Voltage, mV Blue Water*
1	TCO	Ag	+ .085	+ 0.025	- 0.045
1	Ag/TCO	SCE		+ 88	+ 11
1	TCO	SCE		+ 40	- 275
3	↓	↓		+ 120	- 280
4	↓	↓		+ 300	- 200
1	Al	↓		- 700	-1300
1	Al/Ni	↓		- 480	--
2	Evap. Al	↓		- 650	-1500
2	Sput. Al	↓		- 890	-1100
3	HiPur Al	↓		- 740	- 950
3	LoPur Al	↓		- 620	-1250

* Blue Water = 45 parts distilled water to 1 part C. R. Laurence Co., Inc. Glass Cleaner No. 695.