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Additional Study on the Laser Sealing of Dye-Sensitized Solar-Cell-Panels Using V_2O_5 and TeO_2 Containing Glass

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ABSTRACT

The effective glass frit composition used to absorb laser energy and to seal commercial dye-sensitized solar cell panel substrates has been previously developed using V_2O_5-TeO_2-based glass with 10 wt% ß-eucryptite as a CTE controlling filler. The optimum sealing conditions are provided using a 3 mm beam, a laser power of 40 watt, a scan speed of 300 mm/s, and 200 irradiation cycles. In this study, the feasibility of the developed glass frit is investigated in terms of the sealing strength and chemical durability against the commercial iodide/triiodide electrolyte solution and fluorine-doped tin oxide (FTO) electrode in order to increase the solar cell lifetime. The sealing strength of the laser-sealed V_2O_5-TeO_2-based glass frit is 20.5 ± 1.7 MPa, which is higher than those of thermally sealed glass frit and other reported glass frit. Furthermore, the developed glass frit is chemically stable against electrolyte solutions. The glass frit constituents are not leached out from the glass after soaking in the electrolyte solution for up to three months. During the laser sealing, the glass frit does not react with the FTO electrode; thus, the resistivity of the FTO electrode beneath the laser-sealed area remains the same.

Key Words : V_2O_5-TeO_2-based glass frit, Sealing, Laser, Dye-sensitized solar cell, Sealing strength, Chemical durability

1. Introduction

In device modules such as display, optical waveguide for optical communication, solar cell and biochip where joining of panels is required, erosivity problems that adhesives exert on surrounding environments must be solved for longer life-time of devices. When glasses are used as a sealant, application of glass sealant to display and solar cell device modules is very limited despite the excellent hermeticity and chemical durability of the glass itself.[1-3] In general, joining processes using a glass sealant are realized at temperatures of approximately 450-500°C, where such high sealing temperatures can have detrimental effects on temperature-sensitive organic or optical devices constituting the device module.[4-6]

A technique of laser sealing or laser welding in lieu of thermal joining has been recently proposed for the modules composed basically of polymer material panels that are manufactured. This technique employs sealants containing laser-absorbing constituents (carbon black, CNT and other pigments), where a panel substrate is sealed by localized melting through absorption in such sealant of laser energy that was transmitted through the panel substrate.[7-10] Here, the localized melting refers to a phenomenon of melting while temperatures of the surroundings (places away more than approximately 2 mm from the molten part) are being maintained below approximately 150°C. While studies of melting glass sealants by using femto-second laser have been made in part, problems with occurrence of pores or cracks in sealing interfaces have been reported.[11,12] The present investigators have developed V_2O_5-TeO_2-based glass frits in 2014, and reported optimum conditions for laser sealing of commercial dye-sensitized solar-cell-panel substrates.[13] Elements controlling a long life- time of dye-sensitized solar-cell modules include sealing strength of the glass frits for sealing, reactivity with the electrolyte solution and the electrodes. In the present study, use possibility as a sealant for actual dye-sensitized solar-cells has been determined by examining sealing strength shown by the glass frits for sealing, reactivity with the electrolyte solution and the electrodes.

2. Experimental Procedure

The basic composition of glass frits is based on V_2O_5-TeO_2-BaO-ZnO-B_2O_3. Since the V_2O_5-based glasses have a relatively low glass transition temperature and softening temperature due to a low melting point of V_2O_5 (690°C), they are used as a low-temperature sintering aid, and easily absorb near-infrared wavelengths.[14-16] While laser-absorbing glasses with a low glass transition temperature (T_g) and softening temperature (T_d) can be melted by a low laser output, and hence have an advantage of being capable of controlling the surrounding temperatures below a particular temperature upon sealing, they structurally have a disadvantage of crys-

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tallization occurring at a low temperature to reduce flowability. TeO_2 has been added to prevent crystallization of V_2O_5-based glasses and to improve their wetting behavior, where addition was made by substituting 20 wt% of V_2O_5.[13] For powders of each composition, a reagent grade with a purity higher than 99.9% (Kojundo Chemical Laboratory Co., Japan) has been employed. Glass frits with a final average particle size (D_{50}) of 1.98 μm have been prepared by melting in an electric furnace at 1100°C for 30 minutes after undergoing wet mixing and drying of the weighed batch, followed by quenching and wet milling. For control of the thermal expansion coefficient (α) of glass frits, 10 wt% of β-eucryptite ($Li_2O \cdot Al_2O_3 \cdot 2SiO_2$) having a negative (–) thermal expansion coefficient has been added as a filler (D_{50}=4.4 μm) so that the difference in thermal expansion coefficients (Δα) between substrate glasses for dye-sensitized solar- cells was controlled within ±5%. As a substrate glass for commercial dye-sensitized solar-cells, Na_2O-CaO-MgO-SiO_2-based glass (TEC Glass™, Pilkington, USA) with a glass transition temperature (T_g) of approximately 530°C has been used. Paste (solid:vehicle=30:70 in vol%) was prepared by mixing glass powders and the filler together with a vehicle consisting of α-terpineol/2-(2-butoxyethoxy) ethyl acetate/ethyl cellulose (99%, Aldrich, USA) using a 3-roll mixer (50i, EXAKT, Germany), and printed on a glass substrate using a 250-mesh screen in the form as shown in Fig. 1. After drying the printed paste at 120°C based on thermal gravimetric analysis (TGA) results, it was maintained at 300°C for 2 h to remove organic substances, and subjected to pre-firing at 400°C for 10 minutes for laser sealing experiments. The purpose of the pre-firing at 400°C is to minimize pores that can occur in the laser sealing process by removing pores inside the pattern as well as to play a role as a reservoir for injection of the electrolyte through perfect removal of residual organic substances and providing the printed frits with mechanical strength. The glass frits with completion of pre-firing showed a thickness of approximately 20 μm and a line width of approximately 700 μm. For laser sealing, diode laser with a wavelength of 810 nm and a maximum output power of 100 W (Pearl TKS™, nLight, USA) has been employed. The laser sealing was realized at laser output power; 40 watt, irradiation rate; 300 mm/s and irradiation cycle; 200, while the specimen with completion of laser sealing is shown in Fig. 2.[13]

Sealing strengths of the substrates with completion of laser sealing have been measured by using a tensile tester (Nexcade, R&B, Korea) at a load application rate; 2 kg_f/min. Stability of the developed glass frit against a commercial electrolyte solution (Iodolyte AN-50, Solaronix, Switzerland) used for dye-sensitized solar-cells has been analyzed and evaluated for the composition eluted in the electrolyte solution after bulk specimens of V_2O_5-TeO_2-BaO-ZnO-B_2O_3-based glass (10 mm × 10 mm × 5 mm) have been treated in the electrolyte solution(10 ml) at room temperature for 3 months by using Inductively Coupled Plasma Emission Spectroscopy (ICP; Optima 8x00 ICP-OES Spectrometer, Perkin-Elmer, USA). In addition, reactivity with the FTO electrode of the developed glass frit composition has been analyzed by measuring resistances of the FTO deposited substrates before and after laser sealing.

3. Results and Discussion

Experimental results of sealing strength for the specimens with realization of laser sealing are shown in Table 1. In addition to the sealing strength results of the specimens sealed with laser irradiation in the results table, sealing

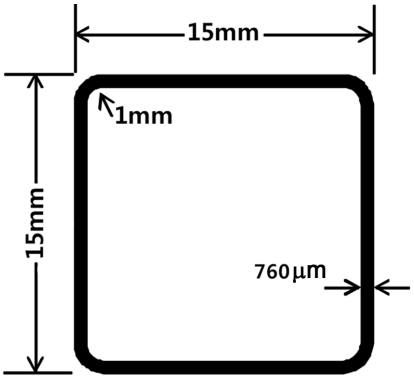

Fig. 1. Screen printing geometry for laser sealing test.[13]

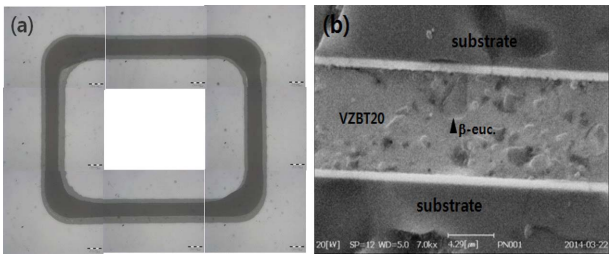

Fig. 2. (a) Optical micrograph of the laser sealed glass panel with laser power; 40W, scan speed; 300mm/s, and irradiation cycle; 200 and (b) SEM micrograph of a cross section of the laser sealed panels showing no pores and cracks.[13]

Table 1. Sealing Strength of Laser Sealed V_2O_5-TeO_2-BaO-ZnO-B_2O_3 Glass Frit. Sealing Strengths of Thermally Sealed Sample, Other Reported Glass Frit and Commercial Sealing Tape are Also Listed

	Laser Sealed[a]	Thermally Sealed[b]	Other Study[c]	Sealing Tape[d]
Sealing Strength	20.5±1.7 MPa	14.3±3.1 MPa	12.3 MPa	23.0±2.3 MPa

[a,b]Present study : V_2O_5-TeO_2-BaO-B_2O_3-ZnO glass
[c]Rivero *et al.*[17] : Asahi Glass Co.
[d]SX1170-60, Solaronix, Switzerland

strength results are also indicated for thermally sealed specimens, as well as for glass frits reported by other investigators[17] and commercial sealing tape (SX1170-60, Solaronix, Switzerland). The sealing strength (σ_{laser}) after laser sealing of the specimens of glass frits developed in the present study were 20.5±1.7 MPa, showing more excellent values than the sealing strength ($\sigma_{thermal}$=14.3±3.1 MPa) for the case of simple thermal sealing of glass frits with the same composition. Fracture surfaces of the specimens after sealing strength experiments are shown in Fig. 3. In the case of laser sealed specimens, the number of pores produced during sealing process was smaller compared with the thermally sealed specimens. This is attributed to the fact that temperatures corresponding to the laser sealing output power were lower than temperatures required of thermal sealing. Also, whereas fracture in the case of laser sealed specimens occurred mainly in substrates, fracture in the case of thermally sealed specimens can be seen to have occurred simply at the interfaces between glass frit and substrate. This implies that firmer joining with the substrate has occurred in the case of laser sealing. It can be seen that strength of the sealant developed in the present study is higher than strength ($\sigma_{other\ study}$=12.3 MPa) of the laser sealants (Asahi Glass Co., Japan) studied by other investigators.[17] Also, sealing strengths of the developed laser sealant show similar values to those of commercial sealing tapes. Thus the developed glass sealant is considered to be more competitive in terms of long-term stability, considering environmental deterioration of commercial polymer tapes.[18]

For thermal fatigue experiments, sealing strengths were measured after repetition of temperature increase and temperature decrease in the temperature interval of -10~80°C for 10 times, respectively, with the specimens with completion of laser sealing, and the results are shown in Table 2. Sealing strengths after thermal fatigue experiments maintained a similar level to the strength values immediately after laser sealing, which is caused by minimization of occurrence of thermal stresses resulting from control of differences in thermal expansion coefficient (Δα) from that of substrate glass below ±5% by adding β-eucryptite to the glass frits.

Chemical durability of sealant with respect to the electrolyte of solar-cells is an essential requirement controlling long life-time of the solar-cells. Experimental results on stability of the developed glass sealant based on V_2O_5-TeO_2-BaO-ZnO-B_2O_3 against electrolyte solutions are given in Table 3. The data shown in Table 3 are measurement results of concentrations of glass component ions in the electrolyte solution processed after glass specimens have been immersed in I^-/I_3^- electrolyte solution for 3 months. Within the range of measurement limits for the ICP equipment employed, none of V, Ba, Te, B, and Zn ions as compositions constituting glasses has been detected, which indicates that the developed glass composition is very chemically stable against the electrolyte solution of solar-cells.

Another item of requirements for the sealant is freedom from reactivity with the FTO electrode deposited on solar cell substrates so as to maintain electrical conductivity of the transparent FTO electrode. For experiments of reactivity between the developed glass frits and the FTO, analysis was conducted through resistance measurements before and after laser sealing by sealing of glass frits having a line width of 700 μm onto a FTO deposited substrate (30 mm × 30 mm) by using laser as shown in Fig. 4. While the number sealed lines was 10 ea, and 10 ea of specimens were used by fabricating the sealed substrates into a size of approximately 30 mm × 3 mm. According to resistance measurements, resistances before (38 Ω) and after sealing (38~40 Ω) were identical, and it can be seen that no reactions had occurred between the glass frits and the FTO in the laser sealing process. Recently, a study of improving electrical connection between the cells in dye-sensitized solar-cells has been conducted by applying Ag electrode onto FTO electrode.[19] However, serious reactivity between Ag electrode and I^-/I_3^- electrolyte remains as a task to be solved.[20] Since there is no reactivity with I^-/I_3^- electrolyte in the case of glass frits developed in the present study, application as a protective film for Ag electrodes is also considered possible.

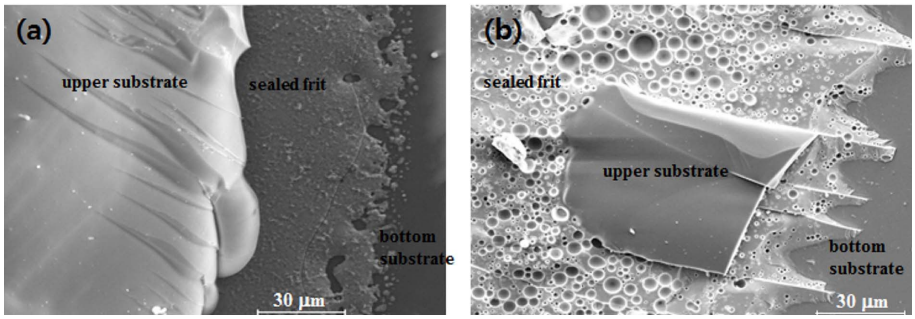

Fig. 3. SEM micrographs showing a fracture surface of (a) laser-sealed panel and (b) thermally sealed panel after tension test.

Table 2. Sealing Strength of Laser Sealed Glass Frit Before and After Thermal Cycling Test

	Before thermal cycling test	After thermal cycling test
Sealing strength	20.5±1.7 MPa	18.8±3.2 MPa

Table 3. ICP Results of Specimen After Soaking in I^-/I_3^- Electrolyte Solution for 3 Months

Sequence No.: 17 — Autosampler Location:
Sample ID: 109 — Date Collected: 2014-10-06 오전 11:28:44
Analyst: — Data Type: Original
Initial Sample Wt: 0.0843 g — Initial Sample Vol:
Dilution: — Sample Prep Vol: 50 mL

Nebulizer Parameters: 109

Analyte	Back Pressure	Flow
All	137.0 kPa	0.70 L/min

Replicate Data: 109

Repl#	Analyte	Net Intensity	Corrected Intensity	Calib. Conc.	Calib. Units	Sample Conc.	Sample Units	Analysis Time
1	B 249.677	39.7	-12.7	-0.067	mg/L	-39.60	ppm	11:29:15
1	Ba 233.527	-1.1	0.3	-0.062	mg/L	-36.86	ppm	11:29:15
1	V 290.880	5529.4	531.1	-0.020	mg/L	-12.01	ppm	11:29:47
1	Zn 206.200	339.4	226.0	-0.059	mg/L	-35.16	ppm	11:29:47
1	Te 214.281	-229.4	-66.9	-0.018	mg/L	-10.69	ppm	11:29:47
2	B 249.677	39.6	-12.8	-0.067	mg/L	-39.88	ppm	11:29:25
2	Ba 233.527	1.2	2.6	-0.057	mg/L	-33.59	ppm	11:29:25
2	V 290.880	5532.2	533.8	-0.020	mg/L	-12.01	ppm	11:29:58
2	Zn 206.200	332.0	218.7	-0.059	mg/L	-35.24	ppm	11:29:58
2	Te 214.281	-236.7	-74.2	-0.019	mg/L	-11.51	ppm	11:29:58
3	B 249.677	40.1	-12.2	-0.065	mg/L	-38.70	ppm	11:29:35
3	Ba 233.527	-0.4	1.0	-0.060	mg/L	-35.82	ppm	11:29:35
3	V 290.880	5520.3	521.9	-0.020	mg/L	-12.05	ppm	11:30:08
3	Zn 206.200	339.9	226.5	-0.059	mg/L	-35.15	ppm	11:30:08
3	Te 214.281	-229.2	-66.7	-0.018	mg/L	-10.67	ppm	11:30:08

Mean Data: 109

Analyte	Mean Corrected Intensity	Calib. Conc.	Calib. Units	Std.Dev.	Sample Conc.	Sample Units	Std.Dev.	RSD
B 249.677	-12.6	-0.066	mg/L	0.0010	-39.39	ppm	0.616	1.56%
Ba 233.527	1.3	-0.060	mg/L	0.0028	-35.42	ppm	1.672	4.72%
V 290.880	528.9	-0.020	mg/L	0.0000	-12.02	ppm	0.021	0.18%
Zn 206.200	223.7	-0.059	mg/L	0.0001	-35.19	ppm	0.050	0.14%
Te 214.281	-69.3	-0.018	mg/L	0.0008	-10.96	ppm	0.478	4.37%

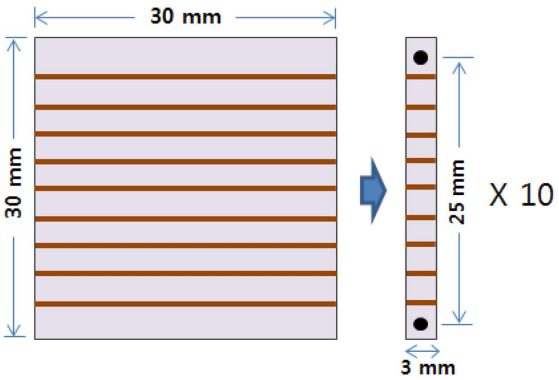

Fig. 4. Test coupon for measuring the resistance of FTO substrate after laser sealing.

4. Conclusion

Localized sealing using laser is essential for sealing of dye-sensitized solar cells with the use of glasses, and the present investigators have reported successful sealing conditions with the use of V_2O_5-TeO_2-BaO-ZnO-B_2O_3-based glass compositions. In the present study, sealing strengths of glass frits for laser sealing, chemical durability against electrolyte and FTO electrode as essential requirements for long life-time of dye-sensitized solar-cell modules have been additionally reviewed, and applicability of the developed glass frits as a sealant for dye-sensitized solar cells has been affirmed.

Sealing strengths of the developed glass frits have shown an excellent sealing strength value; σ_{laser}=20.5±1.7 MPa as compared with general thermal sealing or sealants of other compositions. Pores produced in the glass frits during a laser sealing process were fewer than during a thermal sealing process, and fracture occurred mainly in the substrates rather than the sealants due to strong adhesion with the substrates. In addition, the developed glass frits showed strong chemical durability against the I^-/I_3^- electrolyte solutions and the FTO electrode.

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