Zinc Borosilicate Thick Films as a Ag-Protective Layer for Dye-Sensitized Solar Cells

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ABSTRACT

A zinc borosilicate glass having a low softening temperature of 490°C has been investigated as a protective layer for Ag patterns against chemical reactions with a \( \Gamma^+ \Gamma^- \) electrolyte in dye-sensitized solar cells (DSSCs). A thick glass layer was prepared by the typical screen printing and firing processes to obtain a final thickness of ~5 µm. The chemical leaching performance of the glass layer in the electrolyte revealed that the reactive Ag pattern can be significantly protected by utilizing the low softening protective layer. The electrical resistance of the FTO-coated glass substrate was effectively maintained at a low value of ~27Ω as long as the glass layer was well densified at a sufficiently high temperature of ~520°C. The transmittance of the layer was near 60%, depending on the firing temperature of the glass layer.

Key words: Electrical properties, Borosilicate glass, Substrate

1. Introduction

Dye-sensitized solar cells (DSSCs) have been actively investigated and found to have great commercial potential because of their cost effectiveness, simple fabrication procedure and high conversion efficiency. DSSCs, which typically consist of a semiconductor film as an electrode, ruthenium-based dye, a \( \Gamma^+ \Gamma^- \) electrolyte and a counter electrode, have been the focus of recent efforts to overcome the several technical issues that have been obstacles for their successful large-scale commercialization. One of the important issues to be overcome is associated with the upscale process, which requires the retention of high electrical conduction in the transparent conducting thin films deposited on soda lime silicate (SLS) glass substrates.

Different approaches have been reported for effective electrical interconnections of the resultant cells through improvement of the module design and the manufacturing process. The utilization of a conducting grid as a carrier collector on the transparent electrode has been one of the popular choices. Among many conductors, Ag has been regarded as one of the most promising conductors as the carrier collector because of its low electrical resistance, low dark current and low material cost. However, the well-known corrosion of Ag in the \( \Gamma^+ \Gamma^- \) electrolyte has been an apparent obstacle for the successful commercialization of DSSCs using Ag conductors. Therefore, the passivation of Ag is essential in preventing the undesirable reaction between Ag and \( \Gamma^+ \Gamma^- \) electrolyte, particularly for the long-term stability of the cell.

In this preliminary work, a passivation layer, based on a low softening glass, has been studied for the protection of Ag against the \( \Gamma^+ \Gamma^- \) electrolyte in DSSCs. A zinc borosilicate glass with a low softening temperature was selected as a candidate for such purpose. The firing temperature of the glass and leach duration in the electrolyte are the main parameters of this work.

2. Experimental

A glass batch of zinc borosilicate was prepared by mixing reagent-grade, ZnO (99.9%, Aldrich), B\(_2\)O\(_3\) (99.9%, Kojundo Chem. Laboratory Co., Ltd.) and SiO\(_2\) (99%, Junsei). The glass batch was melted in an uncovered platinum crucible at 1100°C for 1 h, and then the melt was quenched in a roller quencher. For preparing fine glass frit, the quenched glass was ball-milled in ethanol with yttria-stabilized zirconia balls for 20 h. After complete drying, the glass frit was mixed with an organic vehicle composed of ethyl cellulose (Anto chemical Co., Ltd.), α-terpineol (90%, Aldrich), and lauric acid (98%, Aldrich) by using a commercial paste mixer (Daewhatech, PDM-150).

As a next step, an Ag paste was screen-printed on a commercially-available fluorine tin oxide (FTO)-glass substrate via the 400 mesh screen of a grid, and sintered at 520°C for 12 min. The prepared glass paste was screen-printed onto the Ag grid, dried at 120°C, and then fired at temperatures of 480°C, 500°C and 520°C. The printing/drying/firing process was performed twice.
For the leach stability evaluation, the fired samples were immersed in $I^-/I^3-$ electrolyte for various durations of up to 10 hours. The surface and cross-sectional microstructures of the fired samples were observed using a scanning electron microscope (SEM: Model S-4200, Hitachi) and an optical microscope (LV150 BD DIC, Nikon). The variations of the electrical resistances of the FTO layers and the Ag patterns according to firing temperature and leach duration were examined by a multi-meter or a four-point probe. The optical transmissions of the samples fired at different firing temperatures were measured by UV-visible spectroscopy (Jasco, V-570).

3. Results and Discussion

Fig. 1 shows the schematic of a testing sample utilizing glass-passivation on a Ag pattern, which is intended for a large-area DSSC. The Ag pattern is supposed to be screen-printed directly on an FTO-coated SLS glass substrate and subjected to a subsequent firing at ~520°C. The well-densified Ag allows the resistance of the FTO layer to decrease, which is desirable for the large-sized solar cells. Fig. 2 shows a cross-sectional SEM image of the structure developed on the FTO-SLS glass substrate. The Ag layer of ~2 µm thickness is clearly seen with the glass layer fired at 520°C. The thickness of the glass layer is controllable by changing primarily the mesh size of the screen and the viscosity of the paste.

The obtained uniform ~5 µm thickness of the glass layer is very promising when it is considered that the common thickness of typical thick films is >10 µm. The pure glass paste is assumed to wet very well on the surface of Ag during firing and to result in a very uniformly-developed thin layer without apparent microstructural defects such as micropores. As expected, strong adhesion was obtained between the layers of glass and Ag. Due to the limited module thickness of the cells, a layer thinner than 10 µm is preferred.

Prior to examining the effect of the protective glass layer, as shown in Fig. 3, the strong reactivity of the Ag pattern with an $I^-/I^3-$ electrolyte was confirmed in terms of a sheet resistance change at different immersion durations. It is noteworthy that the sheet resistance of the Ag pattern increased drastically after ~1 min and by about 10 times in ~10 min. The significant increment of the sheet resistance indicates that the Ag is progressively involved in a dissolution reaction with the $I^-/I^3-$ electrolyte as the immersion time increases.\(^\text{11}\) Further measurement was not available after 10 min due to electrical disconnection from severe dissolution of the Ag pattern. In an additional leach experiment, the zinc borosilicate glass was found to be quite stable as no detectable weight loss was observed after exposure in the electrolyte for up to 10 h.

The differential thermal analysis (DTA) run of the zinc borosilicate glass showed a glass transition of 452°C and a softening temperature of 490°C. No evidence of exothermic crystallization of the zinc borosilicate glass was observed even up to 550°C. The zinc borosilicate glass with the low softening temperature seems appropriate since its softening temperature is below the target firing temperature of 520°C that is required for the cell fabrication without the warping of the typical SLS glass substrate.

The degree of transmittance of the fired glass was also...
investigated. Fig. 4 shows the optical transmission of the glass fired at different temperatures as a function of wavelength from 300 nm to 800 nm. The pure FTO-SLS substrate showed about 80% transmittance while the transmittance of the glass depends on the firing temperature of the glass layer. The sample fired at 520°C showed transmittance close to ~60%, indicating that the sufficient densification of the glass is achieved without a significant level of porosity at this temperature. Similarly, the two lower firing temperatures of 480°C and 500°C were not found to produce adequate transmittance for cell applications. Note that the glass layer does not exactly match the Ag pattern, thus the excessive coverage away from the Ag pattern reduces the overall absorption area of sunlight if the glass overcoat layer is not sufficiently transparent.

Fig. 4. Transmittance of the as-received, Ag-patterned and glass-coated samples. The glass-coated samples were fired at temperatures of 480°C, 500°C or 520°C.

Fig. 5 shows the changes of electrical resistance of the FTO layer for the samples with the Ag and glass overcoat layers processed at different firing temperatures, but under the same leach condition as a function of immersion time. The electrical resistance of the as-received FTO substrate did not show significant changes. The initial value of ~38.5 Ω was invariably maintained over the duration of immersion. The utilization of the Ag pattern initially improved the electrical resistance to ~27 Ω. Once the leach test began, however, the electrical resistance was significantly increased due to its severe chemical reactions with the electrolyte.11 The electrical resistance reached nearly that of the as-received FTO substrate within ~10 min, at which point the utilization of Ag in the cells becomes useless.

The effect of over-coating of the Ag with glass depends on the firing temperature of the glass layer. The case of firing at the lowest temperature of 480°C does not much improve in keeping resistance low. Increasing the firing temperature to 520°C was the most effective for maintaining the electrical resistance at the low initial value of ~27 Ω over the immersion time range. The intermediate temperature of 500°C, resulted in the abrupt increase of resistance at ~10 min. It is believed that glass densification plays a

Fig. 5. Electrical resistance of the FTO layer for the as-received, Ag-patterned, and glass-coated samples. The glass-coated samples were fired at temperatures of 480°C, 500°C or 520°C.

Fig. 6. Surface microstructures of the glass layer: (a) before the leach test and (b) after 50 h immersion time in the I$_3^-$ electrolyte.
significant role in protecting the Ag pattern from corrosive reaction with the electrolyte.

Fig. 6 shows surface microstructures of the glass overcoat layer fired at 520°C before the leach test (as-fired) and after a 50 h immersion in the electrolyte. The glass surface showed characteristics typical of densified glass, i.e., no porosity and no grain boundary. Presence of such a clean microstructure even after 50 h immersion indicates that the zinc borosilicate processed at the firing temperature of 520°C would be useful as a protective layer for the Ag pattern in a large area DSSC.

4. Conclusions

The effectiveness of applying a glass overcoat layer onto a Ag pattern for the purpose of protecting the Ag pattern from undesirable reactions with the I$_3^-$/I$_2^-$ electrolyte was investigated in this study. The low softening zinc borosilicate glass selected here was very successful in protecting the Ag pattern, as evidenced by the experimental result of maintaining the electrical resistance of a FTO layer at low values of ~27 Ω. The performance of the glass layer was strongly dependent on the firing temperature of the glass, which determines the degree of densification and, thus, the degree of protection over a given period. The application of a glass overcoat layer of ~5 µm would be desirable in competitive large-sized dye-sensitized solar cells.

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REFERENCES