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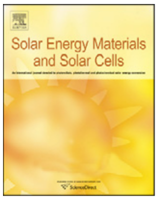

Laser assisted glass frit sealing of dye-sensitized solar cells

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ABSTRACT

A new effective sealing method was developed for application in dye-sensitized solar cells. The sealing method employs a cord of a low temperature fusing glass frit paste that bounds the entire perimeter of the substrate. The glass precursor was heated to its melting point assisted by a laser beam, allowing the two substrates of the cell to be completely sealed. In the present work, the feasibility of this laser assisted glass paste sealing process is investigated and the best laser operating conditions are determined. Different tests were performed to the sealed samples at optimized sealing conditions and conclusions drawn. The glass-sealed samples were compared with results from conventional sealing based on commercial thermoplastics sealants. The results obtained from leakage, temperature and strength tests showed that the glass-sealing technique is better than the conventional method.

1. Introduction

The world yearly consumption of electricity is currently about 17 PWh and it is expected almost to double by 2050 [1]. Moreover, the Gas Crisis at the beginning of 2006 has demonstrated that world, and in particular Europe, is still highly vulnerable with respect to its total energy supply. On the other hand, this energy paradigm is also being hastened by severe climatic consequences of the greenhouse effect caused by fossil fuels combustion and by the environmental effects of several oil spills that have happened in the last years. Therefore, it is imperative to develop technologies to take advantage from energy renewable sources in a sustainable way. Photoelectrochemical effect may greatly contribute to solve this energy paradigm, namely in what concerns the development of devices to convert solar energy into electric energy, mimicking the natural process of photosynthesis [2,3]. Dye-sensitized solar cells (DSCs) are photoelectrochemical cells comprising a photoelectrode of TiO_2 nanoparticles in which organic-metallic dye molecules are adsorbed, electrolyte containing iodide/triiodide redox couple and the platinum counter-electrode. Although several early attempts of using dye-sensitized cells in the conversion of solar energy into electricity, only after the publication of the work by Brian O'Regan and Michael Grätzel in 1991, DSCs started being considered as a low-cost and a promissory alternative to the conventional devices [4]. In the referred work it is described the use of a mesoporous film of TiO_2 with high surface area, allowing to obtain global efficiencies higher than 7 %. Presently, these cells showed a maximum efficiency of ca. 10 %, a modest value when compared with the 25 % from silicon cells, but compensated by their better performance in specific operating conditions [5]. On the other hand, DSCs have a significant lower cost than silicon cells.

In DSCs, the semiconductor is a mesoporous oxide layer composed of TiO_2 nanosize particles that are sintered to allow electronic conduction. Attached to the surface of the oxide is a monolayer of dye molecules (sensitizer), which upon light absorption are promoted into an excited state. As a result, electrons from the ground state of the dye are injected into the conduction band of the semiconductor, giving rise to the formation of excitons (excited electrons) and subsequent charge separation. The free electrons in the conduction band diffuse across the semiconductor towards the external circuit, performing electrical work. Once electrons reach the counter-electrode, typically a thin layer of platinum, they react with the electrolyte that fills the space between the two electrodes, usually a solution of an ionic liquid solvent containing a triiodide/iodide redox system. The original state of the oxidized dye is subsequently restored by electron donation from the electrolyte, which is itself regenerated at the platinum counter-electrode by reduction of triiodide [6–9]. The redox electrolyte therefore allows the transport of electrical charge between the two electrodes of the DSC, closing the cycle.

A basic requirement for all solar cell technologies and in particular for DSCs is the long-term stability. Despite all the efforts to enhance DSCs' performance, long-term stability is still a major issue that limits market implementation of this technology. In fact, for constructing-integrated applications it is expectable that DSCs performance remains stable for no less than 20 years [10].

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The long-term stability problem of the DSC design is directly related to the traditional sealing methods, which use a thermoplastic sealant as Surlyn® or Bynel®. Although these are the most common sealants, other sealing methods are also used in the encapsulation of DSCs [11–16], such as the thermo-compressive glass frit bonding process [17]. This sealing method is quite interesting since it has been demonstrated that lead-free glass frits are thermal and mechanically stable barriers, as chemically inert to the electrolyte and to any conductive metal grid. However, the thermo-compressive method requires the use of high processing temperatures ($>440\,^{\circ}$C) [11] with some mechanical pressure to ensure an appropriate sealing [17], which compromise the dye stability. Therefore, in such procedures the dye must be adsorbed in the semiconductor surface by recirculation after the sealing process instead of the typical dipping process, increasing the manufacturing process complexity.

The present work focuses on the development of an innovative laser-assisted glass frit sealing process. It is proposed a cost-effective, fast and efficient sealing process for DSCs. The sealing material selected is a low temperature melting glass frit. Lasers are used in a wide range of bonding processes [18–20], such as low temperature direct glass bonding [21] and pulsed laser for direct joining glass substrates [18]. However, these processes cannot be used in DSCs devices since photoelectrode and counter-electrode should be spaced by ca. 40 μm. In the present work an intermediate layer is used that acts simultaneously as spacer and as bonding sealing layer. This bonding layer consists of a commercial glass frit paste cord, which melting process is laser-assisted, allowing a relatively low joining temperature. Consequently, a DSC with a hermetic encapsulation can be created. The feasibility of this laser-assisted glass frit paste sealing procedure is investigated and the optimized laser operating conditions are discussed. Different tests were performed to the sealed samples and conclusions are drawn concerning the quality of the implemented solutions.

2. Experimental section

2.1. Materials

The glass paste used (from AGC) is a mixture of a lead-free glass frit ceramic particles with organic solvents and binders. Fig. 1 shows the particle size distribution of the glass paste used, obtained in a Coulter-Counter equipment. Sizes ranged from 130 nm to 3.0 μm. The paste should have a burn out stage before the firing stage to remove the organic components. The paste can be applied by doctor-blading technique or by screen-printing. The glass substrates are from Dyesol (TEC15) and from Solaronix (TCO22-15), soda-lime based and coated with fluorine doped tin dioxide (SnO_2:F or FTO).

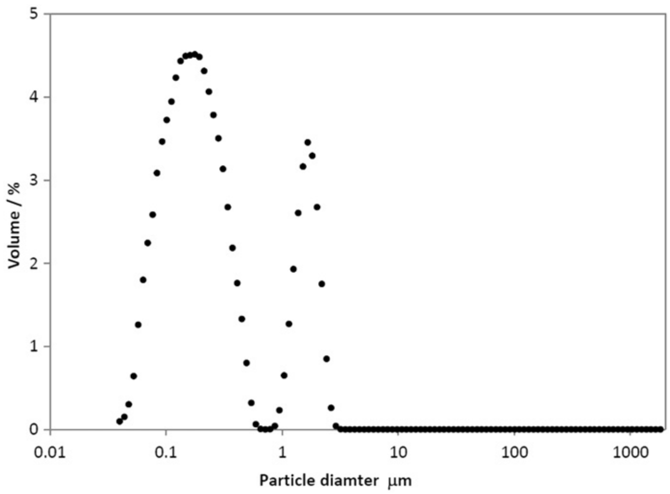

Fig. 1. Size distribution of the glass paste particles.

2.2. Equipment

The glass paste was screen-printed on the FTO glass substrates. The screen is made of a stainless steel 200 mesh/in net coated with a suitable resin.

The sealing process took place in an in-house made "LaserBox" equipment. LaserBox is a closed chamber comprising a laser-scan head and a controlled heating plate. Ytterbium fiber-delivery laser diode array was used. The 2D scan head directs the beam through f-theta lens. The spot can be moved at high speed across the workpiece. The schematic diagram of the experimental setup is shown in Fig. 2.

2.3. Leak and traction experiments

Leak tests were performed using helium gas. An integrated pressurized setup was built to measure pressure drops inside the sealed samples—Fig. 3. It was used as a pressure transducer with ± 2 kPa of repeatability and a maximum pressure range of 1 MPa. The entire set-up was built using stainless steel Swagelok accessories. During the measurements the experimental setup was kept under distilled water at constant temperature (20 °C) to prevent temperature induced pressure changes.

The strength tests were performed using universal traction equipment from TIRA GmbH. The load cell was a Typ 32 500N from HBM.

2.4. Sealing procedure

The glass paste was homogenized on a mill using a zirconium oxide grinding jars with zirconium oxide balls. Glass paste cord rectangles with dimensions of 18.5×8.5 mm^2 and 0.8 mm width were screen-printed on the FTO face of the glass substrates. Printed samples were submitted to a thermal conditioning step at 250 °C for 30 min to drive out the solvents, followed by an organic burn out at 350 °C for 30 min and glazing at 440 °C for 20 min until the surface has a glossy appearance—Fig. 4.

The pre-conditioning step is crucial for obtaining a void-free sealing cord between both FTO-coated glass substrates. Fig. 5 shows two micrographs comparing the final appearance of a glass cord submitted to the referred thermal conditioning with a non-treated glass cord. The voids in the non-treated glass cord are related to the evaporation of solvents and binders initially present in the glass paste.

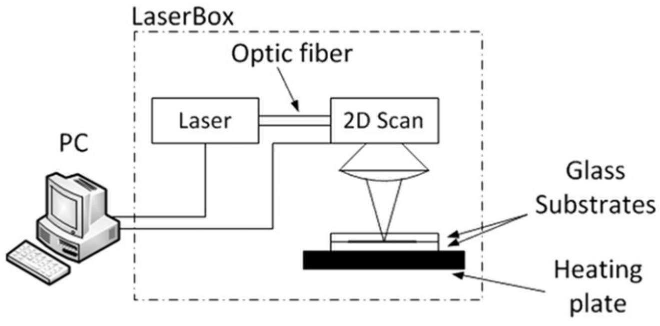

Fig. 2. Sketch of the LaserBox used for sealing DSC devices.