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Dye-sensitized solar cells

Introduction

In the recent energy problems, substitution energy for the fossil fuel has been developed flourishingly. The photovoltaic power-generation, pronoun of clean energy, attracts the attention in various countries in the world. Various specifications of the photovoltaic power-generation system has been built as well as current widely-used silicone-based solar cells. The other hand, IT age become established so that mobile-related devices are popular today. So ensuring power supply and high-performance of devices has continued a fight. In their movement, "Dye-sensitized solar cells" (referred to DSC) attract the attention as the next-generation power supply next to the fuel cell. These solar cells have various advantages that are different from conventional silicone-based solar cells. But power-generation mechanism is the type of chemical reaction so that high-reliability and safety are required. Especially it is said that sealing technology can be the key to produce dye-sensitized solar cells, and many ideas are proposed. This issue mainly provides the performance and characteristics of sealing agents that produce dye-sensitized solar cells.

Contents

1, Method of solar cells

Solar cells are the solar-powered cells as its name suggests, and it is one of our familiar cells. In the thinking of the future energy environment such as limiting the volume of carbon dioxide discharge on global warming, solar cells attracts the attention as the hopeful energy media next to the wind generation. Figure 1 shows the classified solar cells. Like this table, solar cells are classified by semiconductor material: silicone-based, compound semiconductor-based, organic semiconductor-based, and metal-oxide semiconductor-based. Silicone-based solar cells are developed comparatively for a long time, and each of 3 types of silicone-based solar cells has own unique characteristic respectively: single crystal, poly crystal, and amorphous crystal. Well, what kind of principle do solar cells operate or generate based on? Figure 2 shows the principle roughly. As mentioned above, materials of solar cells are semiconductor represented by silicone. Semiconductor is the material used in LSI (Large-Scale Integration), transistor and so on. Solar cells generate the power by 2 types of semiconductors: P-type and N-type semiconductors. In other words, solar cells are the cell that generates by utilizing electronic passing from/to the semiconductor layers, and if only sunshine condition is supplied stably, it is utilized as infinite power supply media. From the point of view like that, solar cells attracts the attention as the next-generation energy source. However, although the utility value is recognized, solar cells to general household have low diffusion rate.

2, What are Dye-sensitized solar cells?

Dye-sensitized solar cells are the cell that dye adsorbed in nanostructure of titanium oxide generates by the light. They are unfamiliar, but their construction technology is familiar to us for a long time. For instance, photo is a familiar technique example that utilizes the sensitization of dye-sensitizing solar cells. The principle of photo printing is the chemical reaction occurred in the time when both the emulsion (silver halide) coated on the film and the dye react to light. The difference from dye-sensitizing solar cells is the difference between titanium dioxide and emulsion, and the principle that the dye absorbs light and generates electron is considered equivalent in a broad sense. On the other hand, plant photosynthesis is also dye-sensitization in the natural world. This is also the same as dye-sensitizing solar cells, and oxygen and plants generate nourishment to grow instead of power-generation. In this way, dye-sensitization technology is widely used in the natural world as well as industrial world, and it is harmonized with nanotechnology that has been in the news so that it can be also said that it is a technology that the new potential is found.

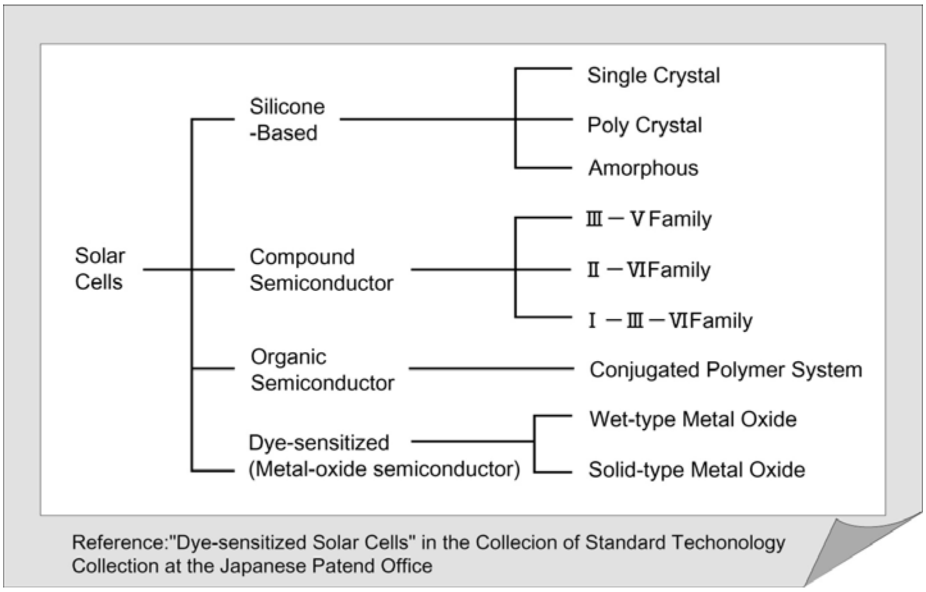


Figure 1, Classification of solar cells

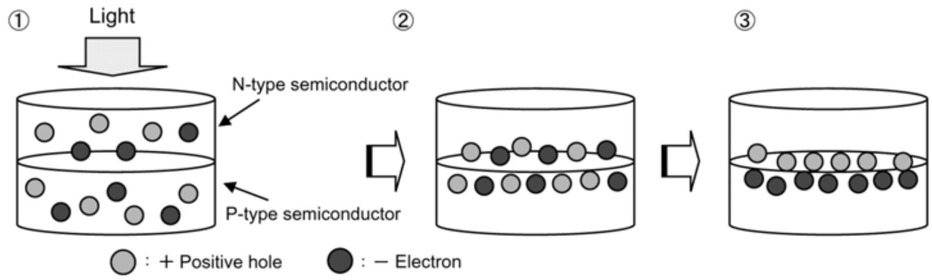
The structure of these solar cells is very simple as shown in figure 3. Well, what is the difference between this solar cell and the solar cells sold in the current market? Compared with the existing silicone-based solar cells, the remarkable point is to make manufacturing facilities simple. Current solar cells use high-purity silicone crystals so that they require a large-scaled manufacturing equipment. Also now in low-costed amorphous silicones, burden for manufacturing facility is heavy and thus manufacturers are limited that can produce and sell cells. Then relationship between price of solar cells and power-generation efficiency is considered. Compared with silicone-based solar cells, power-generation efficiency of DSC (photocarrier generation efficiency) is about 1/10 for small ones. But cost to manufacture DSC is about 1/5 compared with the cost of manufacturing silicone-based so that it takes a short time to depreciate. In other words, compared with the existing solar cells, DSC has a great advantage that it is low-costed, and it can be produced by every manufacturer. In recently announced model houses, their wall surfaces are constructed with DSC. This utilizes the DSC's great feature that power-generation is hard to be affected by incident light angular degree. In the same way, external wall of the buildings may be processed with DSC. It is normal that conventional solar cells are placed on the roof, but DSC can be used in the wall as well as roof so that houses that all power are generated by solar cells can be existed. DSC is also sold as a module unit in the market. DSC is counted because it can be also installed in the hard location to install with silicone-based solar cells. It is expected that DSC has a unique market in its own category, not a substitution of existing solar cells. On the other hand, it is said that the greatest problem for practical use is to ensure a long-term stability. In other words, it is a problem that evaporation of liquid causes performance deterioration because cell is filled with the organic solvent-based electrolyte. It is also required to eliminate the anxiety of the liquid leakage from the view of safety too. Many methods to solve these problems are developed actively.

3, History of DSC

DSC has a long history that belongs to the category of organic semiconductor. As mentioned above, plant photosynthesis provides nourishment by using this principle. When thinking of it, it can be said that DSC is wisdom learned from the natural world by nature. In the public domain announcement at the laboratory level, Tubomura and others at Osaka University announced the DSC principle with zinc oxide on the Nature magazine in 1976 as the oldest one (the relationship between DSC and Japanese were surprising us). But the highest impact announcement is that Graetzel and others announced on the Nature magazine in 1991. This is a basic structure on the current DSC by using titanium oxide and dye, and its patent is acquired in 1988. This basic patent will expire in 2008, and many manufacturers consider its timing as a starting line to industrialization to research and develop currently. This technology has attracted an attention to for a long time in Japan, and it has been researched and developed. Especially research facilities in the university have a cutting edge rather than the enterprises. In foreign countries, venture companies advance their research to scale up dye-sensitized solar cells aiming at practical use, and long-term stability is reported when using multiple unit flotation cells of approximate 10cm x 10cm.

4, Construction of DSC

As shown in figure 3, DSC construction is very compact. Dye-sensitized solar cells use glass substrates with transparent conductive films as an anode (a photoelectrode) that is coated on with nanosized titania particles in paste form and that is sintered at approximate 450 degrees Celsius. Thickness of the titania layer is approximate 10 to 15 micrometer, and titania layer has many nanosized holes so that effective surface area reaches 1000 times or more from the apparent substrate area. When ruthenium bipyridyl complex with carboxyl group is supported to the inner surface of these holes, carboxyl group enables pigments to be combined with the titania surface chemically. On the other hand, as a cathode (counter electrode), platinum is evaporated in transparent conductive films on glass substrates, and electrolyte is filled up between both e electrodes. As electrolyte, solvent of nitrile-based is used, and redox-based of iodine and iodine ion are dissolved as a solute to be elaborated. It is DSC's great characteristic that electron is cycled in such a photochemical reaction. At this point, difference from conventional solar cells is that dye absorbs the lights, that is adsorbed in the semiconductor layer rather than that the semiconductor layer absorbs the lights directly. The amount of light absorption depends on the amount of power-generation, but using dye means that colorful and high architectural solar cells can be designed. It is largely different from conventional solar cells that were black only. Conventional solar cells were monotone and conservative, but appearance of DSC enables solar cells to be colorful and "harmony with environment". Figure 4 shows the conceptual diagram of manufacturing process. When thinking of the process: bonding adherends, sealing, implanting the electrolyte, and sealing, this is similar to LCD panel manufacturing process one decade ago. In other words, even when thinking of manufacturing DSC, it is expected that it can be supported by applying the existing facilities.



1. Pairs of electron (-) and positive hole (+) have occurred when sunshine hits semiconductor.
2. When electron (-) and positive hole (+) come to the joint area of P-type semiconductor or N-type semiconductor, electron (-) is drawn to N-type and positive hole (+) is drawn to P-type respectively. They cannot go back when they are drawn to N/P-type semiconductor because traffic is one way in the joint area.
3. Because electron (-) is collected in N-type semiconductor and positive hole (+) is collected in P-type semiconductor, electromotive force (voltage) between N-type and P-type has generated, if both polarity are connected, electron (-) flows from N-type to P-type, and positive hole (+) flows from P-type to N-type so that current is derived.

Figure 2, Principle of power-generation by solar cells

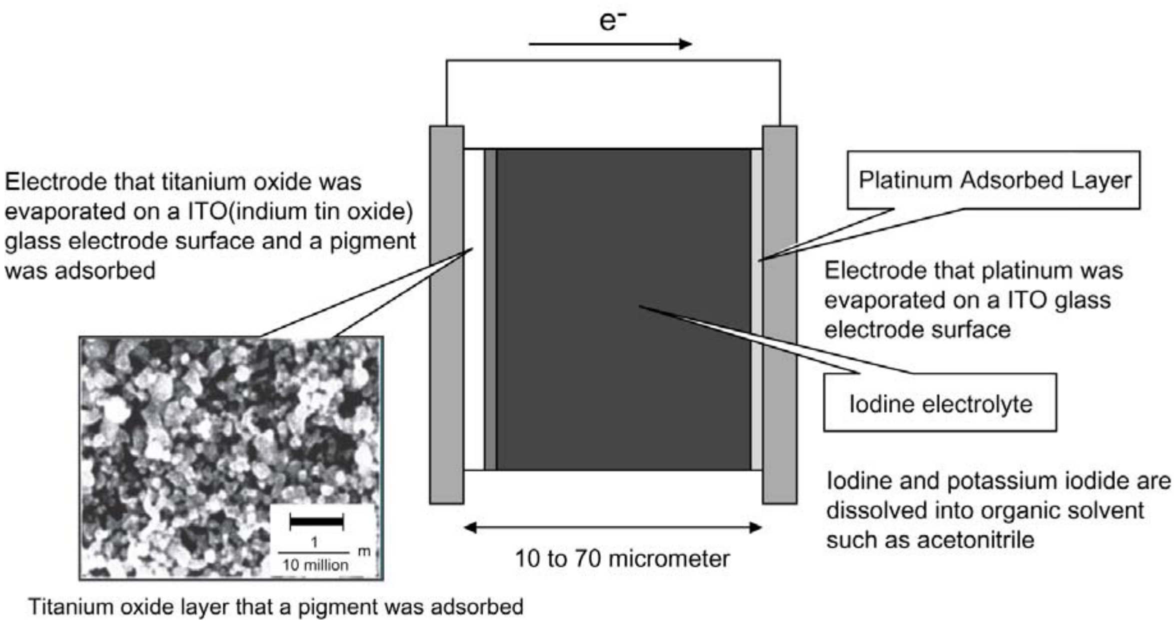


Figure 3, Overview of Dye-sensitized solar cells

5, Prescribed properties of sealants for DSC

As mentioned above of DSC construction, DSC generates the power by chemical reaction between dye and electrolyte. To generate electricity efficiently, it is indispensable to prevent leakage of electrolyte. Electrolyte takes the same role as a blood for DSC, and this drying up means that power-generation is stopped. In other words, to use DSC as an stable power supply, sealing technology is required to prevent electrolyte from leaking. At this point, we discuss a little about electrolyte. Electrolyte consists of high-polarity organic solvents, iodides, and additives. Organic solvent depends on required cell performance, but organic solvent of general nitrile-based is mainly used. Most organic compounds are dissolved because this nitrile-based organic solvent has a high polarity. Therefore in normal high-polymer compounds sufficient resistance cannot be provided, and adhesive property with adherend is given as requirement of the sealing that it is very likely that sealing agents themselves are corroded by electrolyte before sealing, but high adhesiveness means to enhance the polarity of sealing agents so that affinity with electrolyte becomes higher and sealing capability causes to be declined. In other words, relationship between sealing property and electrolyte resistance property is a trade-off. However, reliability of cells is not provided unless sealing is performed. Sealing technology for DSC is required to maintain the performance. In other words, the highest priority as a performance required for sealing agents for DSC is "to control leakage of electrolyte" according to these information. To prevent leakage of iodide itself to outside of the cell as well as volatile, design is required that chemical structure itself of the resin is hard to corrode to polar solvent and iodine.

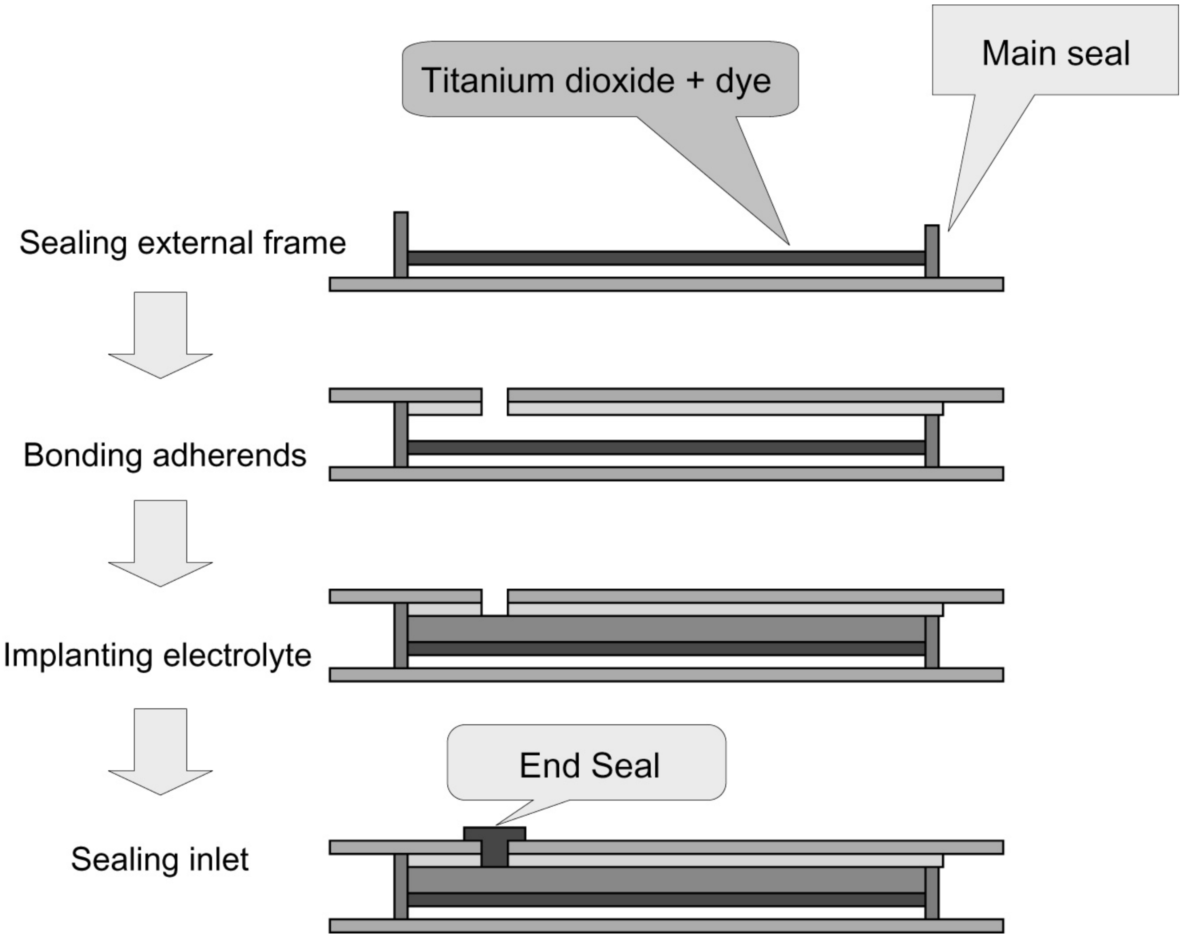


Figure 4, Conceptual diagram of DSC manufacturing process

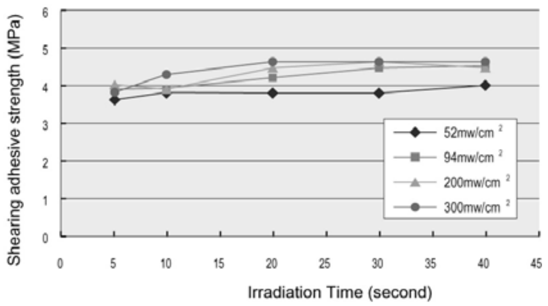
6, Characteristic of sealing agent "31X-101" for DSC

From these backgrounds, we at Three Bond have considered workability and productivity, and light-curing sealing agent "31X-101" for DSC was developed. These characteristic values are summarized as shown in table 1. The design point on the resins is 31X-101's own high electrolyte resistance property. Furthermore as of light-curing property, we considered relationship between shearing adhesive strength and curing intensity, and we found that light at approximate 1000mJ/cm^2 is enough for curing (figure 5). Figure 6 shows the comparison of the electrolyte resistance property between conventional reactive resins and 31X-101. This figure shows that affinity with electrolyte is lower than silicone-based resin, epoxy-based resin, and acryl-based resin. This is originated by 31X-101's resin skeleton. To enhance the electrolyte resistance property, it is required to lower the polarity of resin skeleton. In other words, there is a point that making the polarity of resin skeleton lower than the polarity of electrolyte lowers affinity with electrolyte. Creating "Water and oil don't mix" environment between sealing agents and electrolyte has controlled leakage of electrolyte via sealing agents. Then sealing capability for 31X-101 is considered by using dummy cells. Figure 7 shows how to create dummy cells. To create dummy cells, 31X-101 is coated between two glass substrates, and electrolyte is implanted, the sealing state is created. In this state several durability tests are performed. Results of electrolyte leakage property by UV-ray exposure test for dummy cells that were made in this way, that are summarized as shown in figure 8 to figure 11. Figure 8 shows the results on each environment test about seal width and electrolyte leakage property. This figure shows that if gap is 15 micron (height is 15 micron that sealing agents are squeezed), when seal width is more than or equal to 3mm, electrolyte leakage property is greatly controlled. Furthermore as a result that sealing agent's gap was also considered, as shown in figure 9, we found that narrowing the sealing agent's gap can improve electrolyte leakage control ability. Then we performed the similar tests by changing the types of electrolyte. Figure 10 shows the result. As this result, it is found that electrolyte leakage control ability greatly depends on the types of electrolyte. Especially in propylene carbonate (PC shown in the figure) and gamma-butyrolactone (gamma-BL in the figure) it was found that great depression effect is shown, not depending on the width of sealing agents. As similar consideration, compared with the sealing agents (thermoplastic resin) used in DSC historically, in a result of seal width (3 mm), it was found that 31X-101 is a great sealing performance in the every electrolyte (figure 11).

Table 1, Basic characteristics of sealing agent 31X-101 for DSC

	31X-101	Test method	Remarks
Appearance	Creamy white	3TS-201-01	Visually
Viscosity (Pa・s)	160	3TS-210-02	BH-type, No.7, 60rpm
Specific gravity	0.98	3TS-213-02	Specific gravity cup method
Hardness	55	3TS-215-01	Durometer A
Chemical resitance *1 (%)	2	3TS-620-01	60℃x24h
Premeability *2 (g/m2・24h)	40	JIS Z 0280	60℃x95%RH
Peeling property (MPa)	4	3TS-320-02	Peeling speed of 50mm/min
Elongation ratio (%)	70	3TS-301-02	Peeling speed of 50mm/min

*1: Immersed in acetonitrile, *2: Thickness of 100 micron



[Test condition] Test piece: alkali glass, peeling speed: 50mm/min

Figure 5, Relationship between irradiation time and shearing adhesive strength by UV-ray intensity

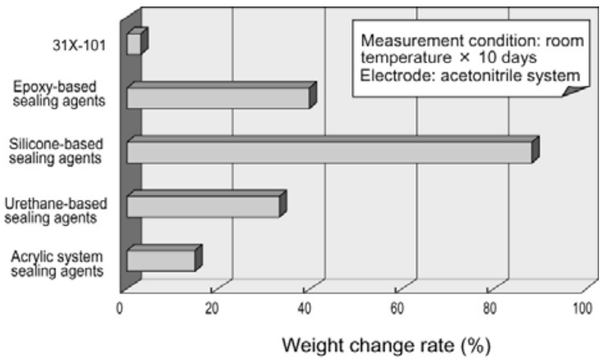


Figure 6, Comparison of electrolyte resistance property on several sealing agents

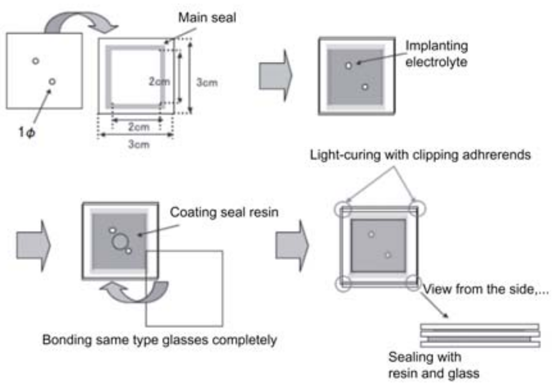
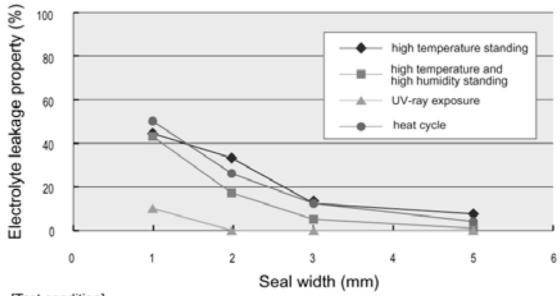
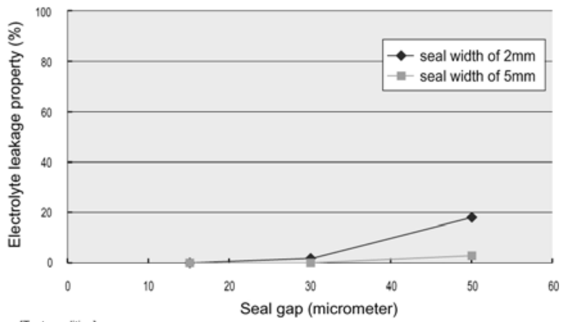


Figure 7, How to create dummy cells



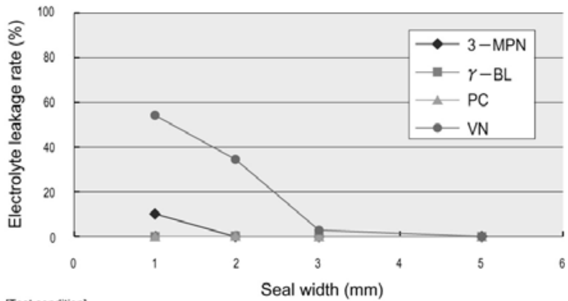
[Test condition]
high temperature standing: 60°Cx96h
high temperature and high humidity standing: 60°Cx95%RHx96h
UV-ray exposure: 48 cycles (102 min. as against fine weather, 18 min. as against rainy weather)
Heat cycle: 200 cycles (30minutes as against -40°C to 90°C)
[Electromagnetic wave]
3-Methoxy propionitrile system (I_2: 0.1M, KI: 0.05M, MePrImI: 0.6M, TBP:0.5M)

Figure 8, Sealing property on several environmental tests



[Test condition]
UV-ray exposure: 48 cycles (102 min. as against fine weather, 18 min. as against rainy weather)
[Electromagnetic wave]
3-Methoxy propionitrile system (I_2: 0.1M, KI: 0.05M, MePrImI: 0.6M, TBP: 0.5M)

Figure 9, Relationship between seal width and seal gap



[Test condition]
UV-ray exposure: 48 cycles (102 min. as against fine weather, 18 min. as against rainy weather)
[Electromagnetic wave]
3-MPN: 3-Methoxy propionitrile, Gamma-BL: Gamma-butyrolactone, PC: Propylene carbonate,
VN: Valeronitrile (I_2:0.1M, KI:0.05M, MePrImI:0.6M, and TBP:0.5M were added into them respectively)

Figure 10, Sealing property on several electrolytes

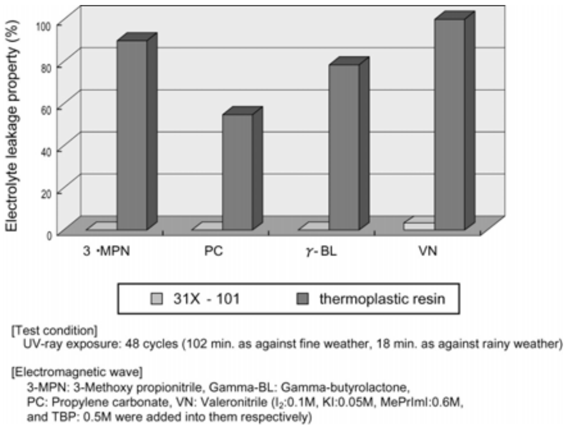


Figure 11, Comparison with thermoplastic resin on several electrolytes

7, Conclusion

DSC is in the news so that mass communication media take it up as well as fuel cells and organic ELs. It will have a long way that DSC is in practical use, but its high design flexibility also enables the applications such as notebook PCs, cellular phones, and PDAs to be greatly expected, and it attracts an attention as a ubiquitous electric power-supply in the mobile age. Three Bond has studied and developed the sealing technology and the seal materials adequate to DSC for many years. We take advantage of them and we hope that they will contribute to the propagation of DSC in the future.

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