

spin-coated on the surface of the N3 dye/TiO₂ electrode and then Au is deposited by vacuum evaporation as the counter electrode, resulting in a sandwich-type DSSC. The cell efficiency was 0.7% under 9.4 mW cm⁻² irradiation, and a J_{SC} of 3.18 mA cm⁻² was obtained under AM1.5 (100 mW cm⁻²) [149]. The maximum IPCE was 33%. The rate of electron injection from OMeTAD into cations of N3 dyes has been estimated as 3 ps, which is faster than that from I⁻ ions [150].

Tennakone and coworkers utilized a *p*-type semiconductor material, CuI (band gap, 3.1 eV), as a hole conductor and fabricated a solid-state DSSC [147, 151, 152]. Acetonitrile solution of CuI is dropped into the surface of the dye-coated TiO₂ film heated at approximately 60°C and then is diffused inside the film. After evaporation of the acetonitrile, CuI is deposited into nanoporous TiO₂ film. Au-coated TCO substrate as the counter electrode is pressed onto the surface of the TiO₂/dye/CuI film. In a system using santalin dye as the photosensitizer, 1.8% efficiency was obtained under 80 mW cm⁻² irradiation [147] and the efficiency reached 4.5% for the TiO₂/N3 dye/CuI/Au system, suggesting the possibility that a highly efficient solid-state DSSC could be produced [151]. In these systems, CuI is considered to be partially in contact with TiO₂, decreasing cell performance owing to the recombination of injected electrons. To increase cell performance, there must be decreased TiO₂/CuI contact. Solid-state DSSCs have been studied using other organic and inorganic hole conductor materials, *p*-type CuSCN [153, 154], polypyrrole [155], and polyacrylonitrile [97].

Quasi-solidification of the electrolyte using a gelator is another method for replacing liquid electrolytes in a DSSC. Gelation can be accomplished by adding gelator into the electrolyte without other changes in the components of the electrolyte. Yanagida and coworkers studied gelation of the electrolyte using L-valine derivatives (Figure 15.14) as a gelator and measured solar cell performance of DSSCs using gel electrolytes [156]. The gelator was added at a concentration of 0.1 M and then dissolved at 90 to 140°C. The gel solution was poured onto the dye-coated TiO₂ film and then cooled. Interestingly, the performance of DSSCs using a gel electrolyte has been almost the same as that using a liquid electrolyte. Good long-term stability of the sealed cell using the gel electrolyte was obtained compared to that of a sealed cell using a liquid electrolyte.

Recently, Hayase and coworkers (Toshiba Co.) reported constructing a highly efficient DSSC using a gel electrolyte [157, 158]. The chemical structure of one of the gelator materials is shown in Figure 15.14. The gelator was dissolved in the electrolyte at high temperature, and consequently the gel solution was deposited on the dye-coated TiO₂ electrode surface and then cooled. One electrolyte composition they reported is a mixture of a gelator shown in Figure 15.14 (0.1 g), 1-methyl-3-propylimidazolium (10 g), I₂ (0.1 g), and 1,2,4,5-tetrakisbromomethylbenzene (0.1 g). Gelation is caused by polymerization between nitrogen and halogen compounds. A high efficiency, 7.3% ($J_{SC} = 17.6$ mA cm⁻², $V_{OC} = 0.60$ V, and $ff = 0.68$), was obtained for an N3 dye-sensitized TiO₂ solar cell using the gel electrolyte under AM1.5 irradiation, compared to 7.8% for a solar cell based on a liquid electrolyte. They concluded that the resistance of the electrolyte did not increase as a result of the gelation because no change of the fill factor was observed. The photocurrent increased linearly with increasing incident light intensity of up to 100 mW cm⁻², as well as a liquid DSSC. This suggests that gelation of the electrolyte does not suppress diffusion of I⁻ and I₃⁻ ions in the electrolyte.