



Hydroxide-Assisted Bonding of Ultra-Low-Expansion Glass

Preparation of bond surfaces is critical to success.

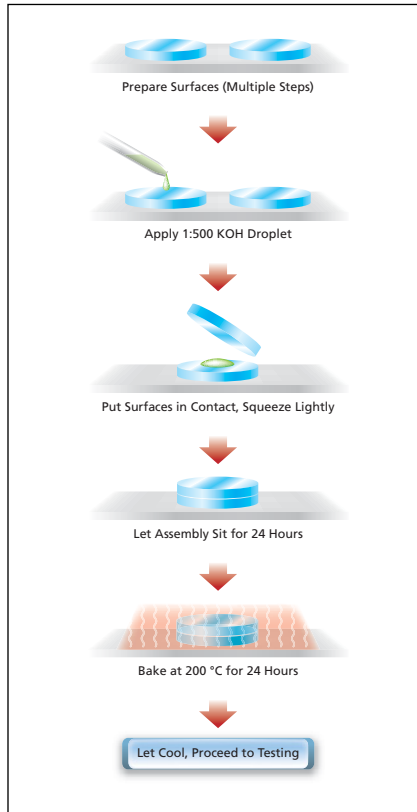
NASA's Jet Propulsion Laboratory, Pasadena, California

A process for hydroxide-assisted bonding has been developed as a means of joining optical components made of ultra-low-expansion (ULE) glass, while maintaining sufficiently precise alignment between. The process is intended mainly for use in applications in which (1) bonding of glass optical components by use of epoxy does not enable attainment of the required accuracy and dimensional stability and (2) conventional optical contacting (which affords the required accuracy and stability) does not afford adequate bond strength.

The basic concept of hydroxide-assisted bonding is not new. The development of the present process was prompted by two considerations: (1) The expertise in hydroxide-assisted bonding has resided in very few places and the experts have not been willing to reveal the details of their processes and (2) data on the reliability and strength attainable by hydroxide-assisted bonding have been scarce.

The first and most critical phase of the present hydroxide-assisted-bonding process is the preparation of the surfaces to be bonded. This phase includes the following steps:

2. Ultrasonic cleaning in successive baths of acetone, methanol, and propanol, using an ultrasound



Two Prepared Surfaces are placed in contact with a small amount of a hydroxide solution at the interface. The assembly is allowed to sit and is then baked. The resulting bond is at least as strong as an epoxy bond.

cleaner that operates at several Megahertz (Megasonics).

3. Treatment in a solution of potassium hydroxide and ammonium hydroxide in an ultrasonic cleaner, at Megahertz frequencies.

Thorough rinsing with deionized water is carried out after each of the above-mentioned steps. The last rinse is followed by ultrasonic cleaning in deionized water, then the cleaned surfaces are blow-dried with ionized air.

After preparation of the surfaces as described above, a droplet of a dilute solution of potassium hydroxide is placed on one of the surfaces, then the surfaces are placed in contact and gently squeezed together (see figure). The resulting assembly is allowed to sit at room temperature for 24 hours, and is then baked at a temperature of 200 °C for 24 hours.

In mechanical tests, sample bonds made by this process were found to have tensile strengths of at least 1.3 kpsi (≈ 9 MPa), where the epoxy bond used to attach the sample to the tensile stress test apparatus broke.

This work was done by Alexander Abramovici and Victor White of Caltech for NASA's Jet Propulsion Laboratory. For more information, contact iaoffice@jpl.nasa.gov. NPO-45247

Photochemically Synthesized Polyimides

Single monomers are polymerized by exposure to ultraviolet light, without heating.

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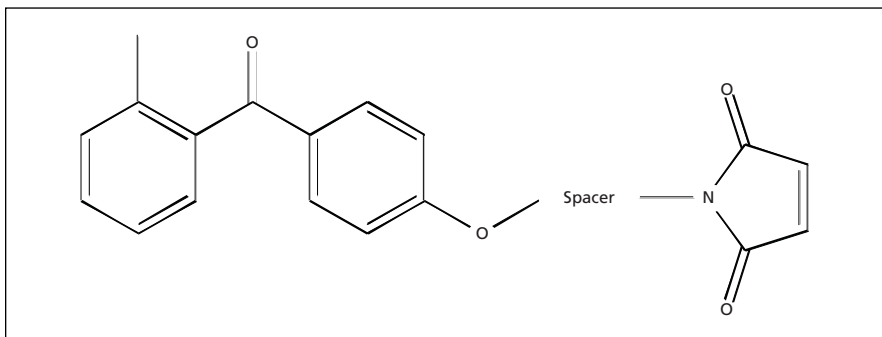
An alternative to the conventional approach to synthesis of polyimides involves the use of single monomers that are amenable to photopolymerization. Heretofore, the synthesis of polyimides has involved multiple-monomer formulations and heating to temperatures that often exceed 250 °C. The present alternative approach enables synthesis under relatively mild conditions that can include room temperature.

The main disadvantages of the conventional approach are the following:

- Elevated production temperatures can lead to high production costs and can impart thermal stresses to the final products.
- If the proportions of the multiple monomeric ingredients in a given batch are not exactly correct, the molecular weight and other physical properties of the final material could be reduced

from their optimum or desired values.

To be useful in the alternative approach, a monomer must have a molecular structure tailored to exploit Diels-Alder trapping of a photochemically generated *ortho*-quinodimethane. (In a Diels-Alder reaction, a diene combines with a dienophile to form molecules that contain six-membered rings.) In particular, a suitable monomer (see figure) contains *ortho*-methylbenzophenone con-



A **Monomer Molecule** suitable for photopolymerization contains a generic spacer group between an *ortho*-methylbenzophenone and a maleimide group.

nected to a dienophile (in this case, a maleimide) through a generic spacer group. Irradiation with ultraviolet light gives rise to a photochemical intermediate — the aforementioned *ortho*-quinodimethane — from the *ortho*-methylbenzophenone. This group may react with the dienophile on another such monomer molecule to produce an

oligomer that, in turn may react in a step-growth manner to produce a polyimide.

This approach offers several advantages in addition to those mentioned above:

- The monomer can be stored for a long time because it remains unreactive until exposed to light.
- Because the monomer is the only active starting ingredient, there is no need for

mixing, no concern for ensuring correct proportions of monomers, and the purity of the final product material is inherently high.

- The use of solvents is optional: The synthesis can be performed using the neat monomer or the monomer mixed with one or more solvent(s) in dilute or concentrated solution.
- The solubility of the monomer and the physical and chemical properties of the final polymer can be tailored through selection of the spacer group.

This work was done by Michael A. Meador of Glenn Research Center and Daniel S. Tyson and Faysal Ilhan of Ohio Aerospace Institute. Further information is contained in a TSP (see page 1).

Inquiries concerning rights for the commercial use of this invention should be addressed to NASA Glenn Research Center, Innovative Partnerships Office, Attn: Steve Fedor, Mail Stop 4-8, 21000 Brookpark Road, Cleveland, Ohio 44135. Refer to LEW-18174-1.

Optimized Carbonate and Ester-Based Li-Ion Electrolytes

This technology can be used in portable electronics, cell phones, and electric vehicles.

NASA's Jet Propulsion Laboratory, Pasadena, California

To maintain high conductivity in low temperatures, electrolyte co-solvents have been designed to have a high dielectric constant, low viscosity, adequate coordination behavior, and appropriate liquid ranges and salt solubilities. Electrolytes that contain ester-based co-solvents in large proportion (>50 percent) and ethylene carbonate (EC) in small proportion (<20 percent) improve low-temperature performance in MCMB carbon-LiNiCoO₂ lithium-ion cells. These co-solvents have been demonstrated to enhance performance, especially at temperatures down to -70 °C. Low-viscosity, ester-based co-solvents were incorporated into multi-component electrolytes of the following composition: 1.0 M LiPF₆ in ethylene carbonate (EC) + ethyl methyl carbonate (EMC) + X (1:1:8 volume percent) [where X = methyl butyrate (MB), ethyl butyrate EB, methyl propionate (MP), or ethyl valerate (EV)]. These electrolyte formulations result in improved low-temperature performance of lithium-ion cells, with dramatic results at temperatures below -40 °C. [See "Ester-Based Electrolytes for Low-Temperature Li-Ion Cells," (NPO-41097) *NASA Tech Briefs*, Vol 29, No. 12 (December, 2005), p. 59.]

Improved low-temperature performance can also be realized with ester-based electrolytes containing high salt concentrations and by using mixed salt formulations — specifically with (a) 1.0 M LiPF₆ + 0.40 LiBF₄ and (b) 1.40 M LiPF₆ dissolved in EC+EMC+MP (1:1:8 volume percent) and EC+EMC+MB (1:1:8 volume percent) solvent mixtures. The rate capability has been observed to increase dramatically at low temperatures (i.e., -60 °C) using this approach. It is anticipated that increased salt concentrations and the use of mixed salt systems will also improve the low-temperature performance characteristics of other solvent blends of carbonates and esters. ["Mixed-Salt/Ester Electrolytes for Low-Temperature Li + Cells" (NPO-42862), *NASA Tech Briefs*, Vol. 30, No. 11 (November 2006), p 66.]

A number of these electrolytes have been demonstrated in both experimental and aerospace-quality, high-capacity prototype cells. In more recent work, these ester-containing electrolytes have been further optimized to provide both good low-temperature performance (down to -60 °C) while still offering reasonable high-temperature resilience. This has primarily been achieved by fix-

ing the EC-content at 20 percent and the ester co-solvent at 20 percent, in contrast to the previously developed ultra-low temperature systems, which have the EC-content and ester-content at 10 percent and 80 percent, respectively. Using this approach, a prototype cell containing a 1.0 M LiPF₆ EC+EMC+MP (20:60:20 volume percent) electrolyte was capable of delivering over six times the amount of capacity delivered by the baseline ternary, all-carbonate blend, and was able to support reasonably aggressive rates at low temperature (-50 and -60 °C). Cells containing other esters also performed well at low temperature, with the lower-molecular-weight, lower-viscosity co-solvents generally yielding better performance at low temperatures.

Although slightly less favorable in terms of electrolyte conductivity, the higher-molecular-weight esters [i.e., propyl butyrate (PB), and butyl butyrate (BB)] are expected to result in cells with more favorable high-temperature resilience (>40 °C), compared to the lower-molecular-weight esters.

This technology has relevance for manned and unmanned space missions, aircraft batteries, and Land Warrior applications, as well as for terrestrial applica-