

## Abstract

Positron annihilation lifetime spectroscopy (PALS) was applied to study the porosity of four highly porous polymers: Amberlite XAD 4, Amberlite XAD 16, Haysep S and Hypersol-Macronet MN 200, all of which have been evaluated for H<sub>2</sub> fuel storage. PALS revealed two types of pores, with average sizes around 2.0 Å and 6.0 Å. It was also determined that the smaller pores have a larger adsorption potential, while the larger pores constitute most of the fractional free volume. At low temperature (77 K), large pores *trap* most H<sub>2</sub> molecules in the condensed gas state, rather than *adsorb* H<sub>2</sub> molecules on their internal wall, as characterized by the Brunauer–Emmett–Teller (BET) method. In addition, it was found that 1) the fractional free volume ( $f_v$ ) of large pores, 2) the uniformity of large pores, and 3) the relative percentage of small pores are all key factors in storing H<sub>2</sub> molecules at a low temperature. Ultimately, the PALS technique, one of the most powerful tools in characterizing micropores at the Å scale, can provide more informational (*e.g.* pore size, number, distribution) and accurate (*e.g.* fractional free volume rather than specific surface area) knowledge on the porosity of materials potentially used for H<sub>2</sub> fuel storage in the future.