Abstract: Based on photo-stimulated discharge (PSD) theory about release of charges from the mono- and multi-levels of traps, two methods on the energy distribution of trapped charges (charge distribution)—step scanning method and combined calibration–scanning method are proposed. The typical polymeric dielectric, low-density polyethylene (LDPE), is selected to be investigated in this paper. The linear relation between PSD current and time at selected wavelengths in LDPE samples indicates that the effective interaction cross sections between the photons and trapped charges depend on the photon energy. It is indicated that both of the largest ratios in charge distributions based on the two methods are around the energy level of 4.97 eV for LDPE. Compared with the step scanning method, the experimental time is extremely shortened and thermal release of trapped charges is decreased in the combined calibration–scanning method, and charge distribution based on combined calibration–scanning method is more reliable.