Abstract：Polyethylene (PE) samples were surface fluorinated for different times in a laboratory vessel. Space charge measurements reveal interesting changes in space charge behavior with fluorination time. ATR-IR analyses suggest an increasing degree of fluorination and fluorinated layer thickness with fluorination time, and SEM images of cross-section of the fluorinated samples give direct information on the fluorinated layer thicknesses. Surface energy calculations indirectly indicate a dramatic increase in permittivity or polarity of the fluorinated layers with different degrees. Open-circuit TSD current measurements show that the fluorinated layers have different charge trapping properties and increasing barrier properties to diffusion of the chemical species from the semi-conductive electrode to the PE with fluorination time. This therefore suggests a decrease in free volume in the surface layer with fluorination time and a corresponding decrease in charge transport. The charge transport properties and thickness of the fluorinated layer are more important to suppress space charge accumulation in the bulk, although high permittivity and deeply trapped charge in the surface layer would reduce the interface electric field and decrease charge injection