Abstract : Linear low density polyethylene (LLDPE) samples were surface oxyfluorinated for different times to investigate the influences of oxyfluorination time on charge injection from carbon black loaded poly(ethylene-co-vinyl acetate) (EVA) electrode and charge accumulation in bulk. Oxyfluorination led to the substantial variations in chemical composition, forming large numbers of various polar groups in the surface layers, depending on oxyfluorination time, as indicated by attenuated total reflection infrared (ATR-IR) analyses. Space charge measurements based on the pressure wave propagation method revealed obvious dependence of the charge injection and accumulation on oxyfluorination time when the samples were submitted to an average direct current field of about 50 kV/mm at 40 °C . Suppression of the charge injection and accumulation by the oxyfluorinated surface layer was enhanced with extending oxyfluorination time. The total amounts of the positive and negative charges within the samples oxyfluorinated for 1, 6, and 13 h were calculated to be around 67, 50, and 29% of the total amount in the original sample, respectively. Diffusion of the volatile byproducts within the EVA electrode into LLDPE was evidenced by the ATR-IR analyses or indirectly by open-circuit thermally stimulated discharge current measurements. The diffusion influenced the charge injection and accumulation by changing charge traps in the surface layer and the field assisted ionization of the diffused volatile byproducts, and was influenced by the surface oxyfluorination depending on the treatment time. The influences of oxyfluorination on charge injection and accumulation were attributed to the remarkable increase in surface layer permittivity and the changes in its charge trap and barrier property to the diffusion of volatile by-products. The change in surface layer permittivity was indirectly evaluated by surface energy calculations.