Abstract: Linear low density polyethylene discs were surface oxyfluorinated for different time to investigate the influences on charge injection from carbon black loaded poly(ethylene-co-vinyl acetate) (EVA) electrode and charge accumulation in bulk under direct current high voltage. The oxyfluorination leads to the substantial variation in chemical composition, forming various polar groups in the surface layer. The charge injection and accumulation are revealed by space charge measurements. Suppression of charge injection is enhanced by extending oxyfluorination time. Diffusion of the volatile by-products within the EVA electrode and its influences on charge accumulation and charge traps of surface layer are evidenced. The suppression mechanisms of the charge injection are largely attributed to the remarkable increase in permittivity, together with the change in charge traps of the oxyfluorinated surface layer.