Abstract: Direct fluorination, as one of the most effective approaches to chemical modification of polymer surfaces, has been widely developed from fundamental researches to industrial applications for about forty years in chemical industry field. However, today, its investigations and applications in adjusting and controlling the electrical properties of polymers are still deficient. The present paper attempts to briefly bring together our study results obtained in recent years and recently, related to the influence of surface fluorination on space charge behavior in polyethylene (PE), and to give a concluding discussion on the correlation between space charge accumulation in PE and its fluorinated layer properties and characteristics. The results show that a very thin fluorinated layer can yield effective charge suppression in the absence of oxygen in the reactive gas mixtures, whereas a very thick fluorinated layer with a high degree of fluorination is needed to achieve the effective charge blocking in the presence of oxygen. Among the electrical factors influencing space charge, charge transport properties of the fluorinated layer are more important than its charge trapping properties and permittivity or polarity to prevent charge injection into the bulk material, although high permittivity and deeply trapped charges in the surface layer would reduce the interface electric field and thus decrease charge injection from the electrodes. The charge transport properties of the fluorinated layer are closely related to its free volume, and oxygen in the reactive gas mixtures has a strong negative influence on the decrease of free volume and thus on the suppression of space charge.