The formation and oxidation of the main discharge product in nonaqueous secondary Li–O2 batteries, that is, Li2O2, has been studied intensively, but less attention has been given to the formation of cathode–electrolyte interfaces, which can significantly influence the performance of the Li–O2 battery. Here we apply density functional theory with the Hubbard U correction (DFT+U) and nonequilibrium Green’s function (NEGF) methods to investigate the role of Li2O2@Li2CO3 interface layers on the ionic and electronic transport properties at the oxygen electrode. We show that, for example, lithium vacancies accumulate at the peroxide part of the interface during charge, reducing the coherent electron transport by two to three orders of magnitude compared with pristine Li2O2. During discharge, Li2O2@Li2CO3 interfaces may, however, provide an alternative in-plane channel for fast electron polaron hopping that could improve the electronic conductivity and ultimately increase the practical capacity in nonaqueous Li–O2 batteries.