The maximum discharge capacity in non-aqueous Li-O₂ batteries has been limited to a fraction of its theoretical value, largely due to a conformal deposition of Li₂O₂ on the cathode surface. However, it has recently been established that additives that increase the shielding of either O²⁻ or Li⁺ will activate the formation of toroidal shaped Li₂O₂, thereby dramatically increasing cell capacity. Here we apply porous electrode theory to electrochemical impedance measured at the Li-O₂ cathode to investigate changes in the surface- and ionic resistance within the pores under conditions where either the surface-mechanism or the solution-mechanism is favored. Our experimental observations show that (i) an additional charge transfer process is observed in the impedance spectrum where the solution-based mechanism is favored; (ii) that the changes in the ionic resistance in the cathode during discharge (related to Li₂O₂ build up) is much greater in cells where the solution-based mechanism is activated and can qualitatively determine the extent of discharge product deposited within the pores of the cathode versus the deposition extent at the electrode/electrolyte interface; and (iii) that the observed “sudden-death” during discharge is a consequence of the increasing charge transfer resistance regardless of whether Li₂O₂ forms predominantly through either the surface- or solution-based mechanism.