Degradation phenomena of La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$/Ce$_{0.9}$Gd$_{0.1}$O$_2$ (LSCF/CGO) cathodes were investigated via post-mortem analyses of an experimental solid oxide fuel cell (SOFC) stack tested at 700 °C for 2000 h using advanced electron microscopy (SEM-EDS, HR-TEM-EDS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Similar studies were carried out on non-tested reference cells for comparison. The analysis focused on the LSCF/CGO cathode and the CGO barrier layer, as the cathode degradation can be a major contributor to the overall degradation in this type of SOFC. SEM-EDS and TOF-SIMS were used to investigate inter-diffusion across the barrier layer - electrolyte interface and the barrier layer - cathode interface. In addition, TOF-SIMS data were employed to investigate impurity distribution before and after testing. HR-TEM-EDS was used to investigate possible phase segregation in the LSCF and to look for reaction between the phases. The results show that phase separation and inter-diffusion across the cathode-barrier layer interface and the barrier layer-electrolyte interface happened mainly during sintering and cathode firing, and to a very little degree during the test period.