In operando Raman spectroscopy is used to study ceramic La$_{0.85}$Sr$_{0.15}$MnO$_{3-\delta}$ electrodes infiltrated with BaO. The aim of this work is to clarify why BaO infiltration reduces the polarization resistance in oxygen containing atmospheres. Prior to the in operando experiments, ex situ X-ray diffraction and Raman spectroscopy reveal the formation of a secondary phase, Ba$_3$Mn$_2$O$_8$, on the electrode. During the in operando Raman investigation of the BaO-infiltrated La$_{0.85}$Sr$_{0.15}$MnO$_{3-\delta}$ electrodes, experiments are performed at 300 and 500 °C with oxygen partial pressure 0.1 atm and with −1 or +1 V Applied potential. A changing electrode surface is observed during operation as the Ba$_3$Mn$_2$O$_8$ secondary phase decomposes and manganese oxide accumulates on the electrode surface during cathodic polarization. The observed changes are reversible. These results suggest that the formation of Ba$_3$Mn$_2$O$_8$ is responsible for the reduced polarization resistance observed at open circuit voltage (OCV) in an oxygen containing atmosphere. Furthermore, the results illustrate the dramatic differences between the electrode surface composition at OCV and during cathodic polarization. Overall, the results highlight the dynamic interactions between minor secondary phases and applied potential, a general effect that may be important for the high-performance frequently observed with ceramic electrodes prepared by infiltration.