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Electroreduction effects in $SrTiO_3$ and Y-stabilized ZrO_2

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Solid oxide cells (SOCs) are key elements for hydrogen-based energy storage in a future sustainable energy system. In order to design reliable devices, a detailed understanding of their potential failure mechanisms is needed. In particular, when SOCs are operated in electrolysis mode, the presence of gradients in the electrical and chemical potential can lead to local reduction or segregation which would limit the lifetime of the cells. Using single crystals of the mixed electronic-ionic conductor $SrTiO_3$ and the ionic conductor Y-stabilized ZrO_2 (YSZ) as model materials for SOC electrodes and electrolyte, we analyze electroreduction effects under vacuum conditions. We demonstrate that in $SrTiO_3$ single crystals, dislocations act as easy reduction sites thus establishing filamentary conductance paths during electroreduction, while in YSZ an inhomogeneous reduction front evolves following the electric field lines. When prolonged electroreduction is applied in Hebb-Wagner type geometry, a stoichiometry polarization of the oxygen activity is established in both investigated materials. In $SrTiO_3$, this leads to the sublimation of Sr from the surface close to the cathode leaving behind nanoporous TiO_x thus revealing a significant degradation mechanism which has not been considered in detail before. Also in YSZ, the ongoing electroreduction results in segregation phenomena related to the evolution of new oxygen-depleted ZrO_x phases on the nanoscale eventually altering the oxide's properties irreversibly.