In this work, the oxygen electrode material is the LSM-ScSZ (scandium stabilised zirconia) 50-50 (by weight) composite which was screen-printed on the dense electrolyte and fired at 1100°C. Since the focus of the study is the cathode material for CO₂ electrolysis, the oxygen electrode was kept identical for all the SOECs fabricated. The electrochemical performance of the LSM-ScSZ oxygen electrode working at OCV in the range of 900-750°C is revealed in Figure S1 from a three-electrode SOEC geometry as illustrated in Figure 1. Compared to the fuel electrode, the impedance from this oxygen electrode is negligibly small.
In Figure S2(a), the durability of the 0.5 wt% Pd-GDC co-impregnated LSCM cathode SOEC working in varying atmospheres at 900°C for H₂O-CO₂ co-electrolysis as well as for CO₂ electrolysis is presented. The cell potential variations with operation time was recorded at a constant current density of -0.15 A cm⁻². The SOEC was firstly operated in H₂O-H₂-CO₂-CO 25-25-25 mixture for roughly 66hrs, during which obvious degradation in cell potential can be observed in Figure S2. The impedance spectra recorded during this operation is exhibited in Figure S2(b). Apparently, the electrolysis performance degradation observed in the first 66hr in H₂O-H₂-CO₂-CO 25-25-25-25 mixture is mainly from the increased ohmic resistance with time. After the first 66hrs, the SOEC was operated in H₂O-H₂-CO₂-CO 20-30-25-25 atmosphere at -0.15 A cm⁻² for a short period then in H₂O-H₂-CO₂-CO 15-35-25-25 atmosphere at -0.15 A cm⁻² for roughly 70hrs. The cell potential gradually stabilises with slight degradation in these periods, which is supported by the impedance data record during these operations. Finally, the cell was operated in CO₂-CO 50-50 mixture for CO₂ electrolysis for ~23hrs, during which a stable potential can be seen as shown in Figure S2(a). The data for this period of operation is explained explicitly in our manuscript.

Pulses (increases in potential) are detected to appear regularly in the co-electrolysis operations, and with reducing steam concentration in the fuel gas mixture, the time gap between two pulses increases, i.e. the frequency of pulse decreases. The speculation for these phenomena is the employment of an inefficient steam delivery. Cold point probably emerges on the gas line which causes condensation of steam, in this case, the steam amount carried into the cathode chamber increases and the cell resistance enlarges. When reducint the steam content, the condensation of steam happens less frequently. No pulses show up when operating the cell in CO₂-CO gas mixture in Figure S2, which confirms the above assumption.

![Figure S2](image_url)

Figure S2 (a) Stability measurements from the 0.5 wt% Pd-GDC co-impregnated LSCM cathode SOEC working in varying atmospheres at 900°C with the cell potential recorded vs. time at a constant current density of -0.15 A cm⁻² in a galvanostatic operation (The fuel gas composition of black circle is H₂O-H₂-CO₂-CO 25-25-25-25, with red triangle as H₂O-H₂-CO₂-CO 20-30-25-25, green square as H₂O-H₂-CO₂-CO 15-35-25-25 and purple diamond as CO₂-CO 50-50) and (b) the impedance behaviour recorded during the first 66hrs durability measurement.