SOFC Degradation Issues: Lessons Learned from FCH-JU Endurance

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Combining updated experimental and modeling approaches, EPFL in collaboration with Endurance partners advanced the knowledge in SOFC stack degradation understanding and description.

On the anode side, the Ni grain growth with time is captured and quantified using 3D microstructural acquisition (FIB-SEM) and analysis. Average grain growth is +30% within the first 1000-2000h of operation (780°C) and then constrained by the YSZ backbone. Concomitantly, the TPBL reduces by ≈40%. This contributes to a gradual, limited performance loss that flattens out with time but does normally not lead to end of life.

A new microstructure analysis and quantification concept was coined, “accessible” TPB, considering that not every TPB point is equivalent but depends on the ionic resp. electronic conducting paths (thickness, tortuosity, constrictions) from this point leading to resp. the electrolyte and the gas interfaces. It was noted that, within a representative anode volume, only few segments of the composite may carry a large portion of the overall current passing this volume, showing the structure’s potential vulnerability e.g. in case of microcracks interrupting such paths. Internal microcracks were clearly evidenced e.g. following a redox cycle.

Microcracks were also observed to occur in the LSFC-CGO cathode composite. The effective conductivity within cathode phases was lowered by more than 1 order of magnitude compared to the solid bulk. Furthermore on the cathode side, Gd and Ce from the CGO compatibility layer were found to diffuse into YSZ and form a solid solution at the interface (no new phases), likely affecting the ohmic drop. Mobile Sr from LSCF migrating through pores in the CGO forms $SrZrO_3$ precipitates at the CGO/YSZ interface. This process already occurs during sintering and further continues during operation. Its constricting effect on current flow is likely limited, however.

Concerning $MnCo_2O_4$ coated metal interconnect, Fe from the steel diffuses into the protective coating, densifying the coating and slightly altering its conductivity; the main effect, though, may be to cause a thermal mismatch. Furthermore, silica layers were detected at the steel/scale and scale/protective layer interfaces, which likely lead to ohmic increase with time as well (in addition to the scale itself).

Stacks seals differed in degradation extent between inlet and outlet of the stack, due to the different gas compositions at these locations. Yellow $BaCrO_4$ layers were clearly observed at the seal (Ba-containing) -MIC (Cr-containing) contacts. Seal porosity formed due to the volatility of some seal elements; seal porosity was further clearly affected by polarization.

With new dedicated equipment (4-point bending strength, creep), thermomechanical properties of SOFC stack materials were determined. At operating temperature, the anode strength is almost divided by 2 with respect to the ambient temperature value (from 280 MPa to 160MPa), and the Weibull modulus reduced (from ≈10 to ≈7). A full thermomechanical model of the stack repeating unit (SRU) was established, using the actually measured properties on samples from real production batches (SOLIDpower) in the modeling. The deformation of the MIC cassette was highlighted, leading to potential contact loss areas, especially following thermal cycling.

Good progress was achieved in identifying the different processes (6) governing SRU behavior, with characteristic impedance frequencies attributed. Overall, an updated lifetime predicting model captured the overall trend of stack degradation.

Summarised, current understanding leads to the belief that continuous stack performance degradation with long term operation stems from the incremental addition of cumulating processes (Ni growth and TPB loss, scale formation, $SrZrO_3$ interphase formation, sealing porosity, ..), without these necessarily leading to end-of-life (on the contrary, rather flattening out with prolonged operating time), and that accidental, sudden, or eventual stack failure is likely rather due to thermomechanical issues, provoked either by cycling or by local microcrack formation at vulnerable zones within the electrode microstructures or by progressive contact loss between the constituting layers.

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