Accelerated tests, early prediction and modelling tools

SOEC durability: post-analysis from a 11'000h operated short stack

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A six-cell stack from SOLIDpower was operated for 11'300h in steam electrolysis mode at 710°C. After initial severe degradation (+8%) over the first 2000h at -0.6A/cm² and 50% steam conversion – tentatively attributed to Ni grain growth and interconnect corrosion – a steam supply interruption occurred, leaving applied cell voltages at 2V for ca. 1h. After this event and restoring team supply, current was reduced to -0.5 A/cm² (steam conversion 42%). Interestingly, performance recovered and the stack was continuously operated thermoneutrally for another >8000h with low degradation (<0.5%/kh). After cooldown, 2 cells from the 6-cell stack were selected for detailed post analysis: a border cell (no.1) that showed slightly higher voltage loss and a center cell (no.4) that showed average voltage loss. Cells were cut, embedded and polished mainly for SEM-EDX observation at zones of interest.

On the fuel electrode (Ni-YSZ) side, substantial Ni depletion within 5 µm of the electrolyte interface was clearly seen. This was specifically confirmed by comparing zones from the active region with those located under the sealing, which had carried no current and remained free of Ni depletion. The coarsening of Ni enhanced in high humidity conditions thus caused a displacement of Ni from the TPB to the inner part of the electrode through volatile $Ni(OH)_2$. This implies a growth of the effective electrolyte thickness and a reduction of electrochemically active TPB, which leads to a less active Ni-YSZ region. Compared to another stack operated for 1500h, showing no degradation, no Ni depletion was seen. In addition, the 11000h stack showed significant Si trace contamination at the electrolyte interface.

The YSZ electrolyte close to the air electrode showed distinct nanocavities, generated from the mass transport of species with different diffusion coefficients under a gradient of electrochemical potential. The orientation of the YSZ grains seems to have an influence on the depth of these void formations, implying also a different contact resistance. Clearly this process mechanically weakens this interface. The portion of electrolyte material detached from these voids migrated and re-deposited in form of a dense layer at the interface with the GDC layer. YSZ and GDC formed a mixed layer about 1 µm thick. In addition, Sr inclusions (≈0.5 µm thick) formed a dendritic pattern in contact with pores and YSZ at this interface. Further to a distinct Sr peak (4at%), coincident with $SrZrO_3$ formation, this interface also showed a Cr accumulation (2at% peak). Compared to the 1500h operated stack, similar Sr and Cr peaks were seen (but to a lower extent), yet this stack had not indicated any performance loss.

Summarised, observed degradations on a stack operated in electrolysis conditions are very different (aggravrated) from those seen in fuel cell operation. Nonetheless, despite evident materials alterations seen after >11'000h in steam electrolysis (and even after 1500h), this did not translate to significant performance loss for about a year of continuous operation.

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References

[1] Post-test Analysis on a Solid Oxide Cell Stack Operated for 10,700 Hours in Steam Electrolysis Mode, Rinaldi, G., Diethelm, S., Oveisi, E., Burdet, P., Van herle, J., Montinaro, D., Fu, Q., Brisse, A., *Fuel Cells* (2017), in press.