Phase transformations in zirconia upon electroreduction

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Electroreduction in yttria-stabilised zirconia (YSZ) represents a long-standing scientific challenge with direct implications for both the reliability of solid oxide electrolysis cells and the processing of advanced ceramics through flash sintering. Under sufficiently high electric fields and reducing conditions, transparent and purely ionic conducting YSZ undergoes dramatic electrocoloration and eventually transforms into a mixed ionic-electronic conductor with metallic-like behaviour. Despite decades of research, the microscopic mechanisms governing this transition and the associated structural evolution remain unresolved.

Here, we present a comprehensive investigation of electroreduction in single-crystal YSZ by combining operando electrical characterisation with microscopy and spectroscopy. The results reveal a sequential transformation process consisting of three distinct stages [1,2]. The first stage involves a reversible electrocoloration accompanied by the emergence of characteristic blackening fingers propagating through the crystal. In the second stage, electroreduction accelerates through the formation of mixed ionic-electronic conducting pathways. Finally, a runaway-type reduction process occurs, driving irreversible morphological transformations and filamentary phase formation near the cathode surface.

High-resolution scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy uncovers previously unreported oxygen-deficient phases in the heavily reduced regions [3]. Belt-shaped features beneath the sample surface exhibit a stoichiometry close to $(Zr,Y)_{8.6}O$ and are embedded within a surrounding oxygen-depleted matrix approximated as $(Zr,Y)_2O$. In addition, a chequerboard-like surface morphology is observed and is attributed to strain relaxation mediated by dislocation glide during extreme reduction.

These findings provide new insight into the progression from electrocoloration to heavy electroreduction in YSZ and establish a direct link between electrochemical loading, defect evolution, and phase instability. The results further demonstrate that harsh operating conditions relevant to steam electrolysis can induce irreversible degradation of the electrolyte, ultimately compromising ionic transport efficiency and long-term device performance.

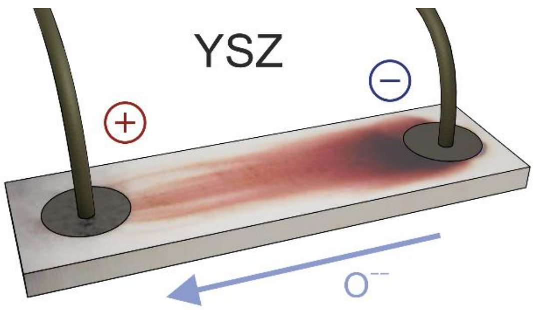

Illustration of the blackening process in YSZ upon electric polarization

References

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[3] C. Rodenbücher, D. Wrana, B. R. Jany, G. Cempura, P. Indyka, A. Kruk, K. Szot, F. Krok, and C. Korte, Sci Rep **16**, 12064 (2026).