Y. Matus,* L. C. De Jonghe,* X.-F. Zhang, S. J. Visco and C. P. Jacobson
Materials Sciences Division
Lawrence Berkeley National Laboratory
and
*Department of Materials Science and Engineering
University of California at Berkeley
Berkeley, CA 94720, USA

ABSTRACT

Yttria stabilized zirconia (YSZ) electrolytes, subjected to high current densities, develop significant damage. This paper characterizes the damage that develops from the anode side, in YSZ used in an oxygen pump configuration. The damage is in the form of vacancy loops, precipitates formed on dislocations, pore development, and grain boundary fracture. The damage initiates at elevated current densities, well below the decomposition potential of YSZ. A mechanism, involving mobile oxygen interstitials, is proposed.

INTRODUCTION

Zirconia electrolytes are susceptible to damage formation and disintegration when subjected to current passage. Direct electrolytic decomposition has been observed above the reduction potential e.g. by Weppner, near 2.2 V, at 1000°C (1). When the cathode has been partially or completely blocked, darkening of the zirconia electrolyte is observed, well below the decomposition potential, at sufficient current densities (2, 3). In this case, an internal divergence in the oxygen vacancy flux results because of electron injection form the negative electrode.

In the present case, we considered current passage through YSZ with non-blocking platinum electrodes in a simple oxygen pump configuration, and found damage formation emanating from the anode (i.e. the oxygen exit side) at high current density. We report on the nature of the damage, its possible mechanism of formation, and consider its potential relevance for fuel cells.

EXPERIMENTAL

500 μm thick zirconia discs were prepared from 8YSZ Tosoh powder, by die pressing at 40 MPa and sintering in air, at 1400°C. The discs were near theoretical density. Platinum electrodes were applied from Pt paste, and fired on at 950°C, to create a symmetrical configuration. The cells were held at 1045°C in air, at a nominal electrode current density of 4.5 A/cm², and the I-V evolution of the anode and cathode was recorded.
Figure 1. Experimental setup, and voltage evolution at a constant current of 4.5 A/cm$^2$, at 1045°C.

The experimental setup is shown schematically in Figure 1, together with the recorded I-V characteristics. After about 2 hours, the onset of a rapid rise in the anode-side resistance, corresponding to V1 in Figure 1, was observed. Note that the onset of the anodic resistance rise is well below a voltage where direct electrolytic decomposition could occur. A fracture cross section, Figure 2, shows that the fracture mode in the zone emanating from the anode, changed from transgranular in the unaffected lower side of SEM micrograph in Figure 2, to intergranular in the damage zone. The cathodic-side resistance, V2, remained essentially unaffected.

Figure 2. Anode side damage development.

After the conclusion of the experiment, the damage in the electrolyte was studied further by transmission electron microscopy. Dislocation decoration (Figure 3) and grain boundary pore (Figure 4) were developed.
Figure 3. Dislocation decoration by current-induced defects.

Figure 4. Grain boundary pore decoration and dislocation activity.

Figure 5. Extensive pore formation and grain boundary fractures.
More severe degradation involves the extensive formation of pores, both inside the grains and on the grain boundaries, as well as intergranular fracture, Figure 5. At some of the grain boundary fractures, a residue could be found which, upon focused EDAX analysis, showed to be a highly oxygen deficient material, likely a mixture of zirconium metal and zirconia, with a \( \text{Zr/Y} \) ratio that was approximately equal to that of the bulk grains, as shown in Figure 6.

![Figure 6. Zirconium at grain boundaries, with strongly lowered oxygen content. The \( \text{Zr/Y} \) ratio is approximately constant.](image)

**DISCUSSION**

The dislocation decoration and pore formation require a damage development mechanism that operates at relatively high current densities, but is not caused by direct electrolytic decomposition. Pore formation must be associated with the generation of excess vacancies. Also, since the damage emanates from the anode, electron injection cannot be invoked as leading to a vacancy flux divergence. It is thus proposed that the damage at high current density develops as a result of a oxygen interstitial partial current. A plausible defect reaction may be described by

\[
4\text{O}_0 + \text{Zr}_z \rightarrow 4\text{O}_i^* + 2\text{V}_0^* + (\text{V}_z, 2\text{V}_0)^* \downarrow + \text{Zr} \downarrow
\]

where the agglomeration of the \( (\text{V}_z, 2\text{V}_0)^* \) complex results in dislocation decoration and pore formation.

At low current densities, it would be expected that the oxygen interstitial-vacancy pair would be almost immobile, and thus of no consequence. However, if this pair dissociates at high currents, and the oxygen interstitials are swept to the anode, then reaction could occur.

It is possible that this phenomenon may also be activated in fuel cell electrolytes that operate at high power density (and hence at high current density). Some indications of a switch from transgranular fracture to intergranular fracture in YSZ and ceria-based fuel cells, has indeed been observed.
CONCLUSIONS

Damage, emanating from the anode rather than the cathode, can develop in zirconia electrolytes at high current densities with non-blocking electrodes. The damage can be severe at high current densities, leading to grain boundary pore formation and fracture. It is possible that similar damage may develop to a lesser degree at lower current densities in solid oxide fuel cells operating at high power. This degradation phenomenon may put an upper limit on the current densities at which oxygen pumps and fuel cells may be operated.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, National Energy Technology Laboratory. The National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory is thanked for making its facilities available for this study.

REFERENCES

1. W. Weppner, J. Electroanal. Chem., 84, 339-350 (1977).
2. J. Janek and C. Korte, Solid State Ionics, 116, 181-195 (1999).
3. X. Guo, Solid State Ionics, 99, 143-151 (1997).