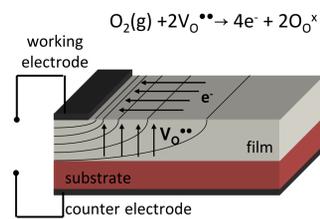


Abstract

The energy conversion efficiency of solid oxide fuel cells (SOFCs) can be improved by facilitating the oxygen reduction and exchange reactions at the cathode surface. Owing to the complexity of standard porous cathode structures, thin film cathodes were prepared by pulsed laser deposition as model surfaces. The goal of this research was to understand the sheet resistance and performance of these model surfaces under applied cathodic polarization in relation to chemical and structural changes.

The applied cathodic potential, which drives the oxygen reduction reaction, is limited to short distance from the metallic current collectors (CCs). The cell resistance (i.e., performance) and electrochemical stability are a function of the quality and geometry of the CCs in contact with the film surface. The extent of surface polarization in LSM and LSCF films is compared to investigate the effect of transference number and the performance stability is considered in terms of CCs and film morphology.

Background and motivation



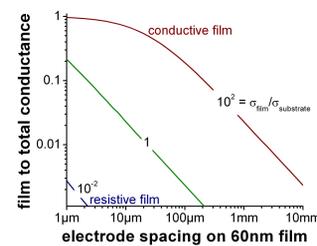
Schematic representation of equipotential lines between WE and CE.

We have hypothesized the extent of this phenomenon will be dependent on the ratio of ionic to electronic resistance in the film. Temperature, film thickness, and materials properties will therefore be the primary parameters affecting the surface potential driving oxygen reduction.

Furthermore, one must decouple the stability of the surface electrodes (i.e., platinum) from the stability of the thin film cathodes for long term polarization investigations.

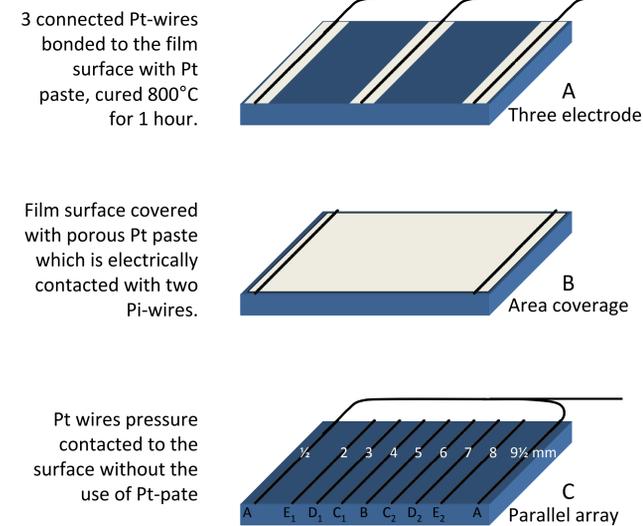
This study experimentally determines the extent of activated surface regions laterally from Pt-surface electrodes as well as electrode stability.

Electrochemically active in situ surface characterization (e.g., X-ray Spectroscopy and TXRF) require exposed surfaces unimpeded by electrodes. Electronic sheet resistance of very thin films is limited electrical current flow. Large lateral potential drops relative to the WE are observed when utilizing surface electrodes. This has been modeled in recent work by Lynch and Liu [1].



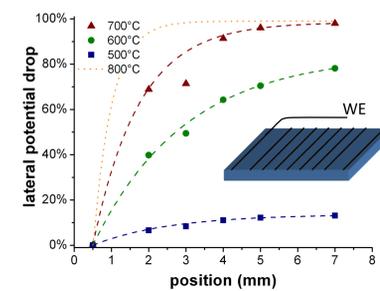
Calculations based on the modified Farnell equation [2].

Experimental electrode geometries



Surface polarization relative to the counter electrode

60 nm (011) LSM / (111) YSZ

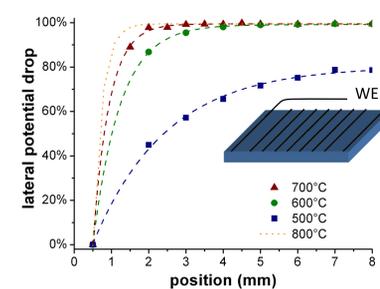


The potential decreases at elevated temperatures with distance from the WE (left): qualitatively consistent with the ASR analysis (above).

$t_{ion}(LSM) \rightarrow 0$: appreciable activated surface area, especially at low temperatures.

Lateral ASR dependence (right) shows edge effects as $x \rightarrow 0$ or 10 mm and significant variability in contact quality.

60 nm (011) LSCF / (111) YSZ



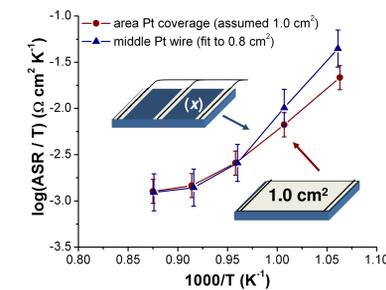
$t_{ion}(LSCF) > t_{ion}(LSM)$: LSCF exhibits a rapid drop in surface polarization laterally from WE.

Polarization between two parallel WE wires (right) is consistent with exponential drop observed for single wire (left).

60 nm (001) / GDC / (001) YSZ orientation shows similar results.

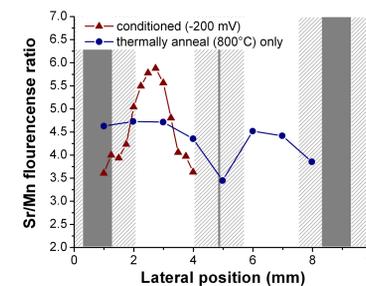
Area specific resistance (ASR)

60 nm (011) LSM / (111) YSZ



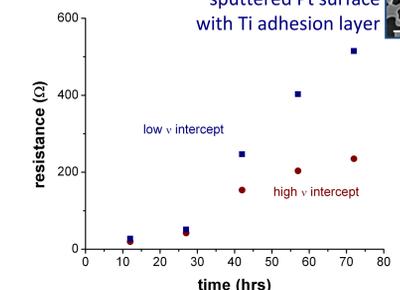
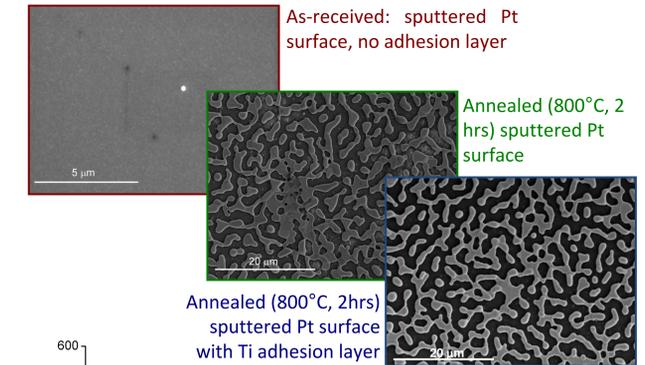
The ASR is assumed to be constant for any electrode geometry. The activated area (x) of "A" is estimated by fitting to ASR of known area from "B", i.e., $x \approx 0.8$ cm². The activated surface area extends ~ 0.8 mm from the WEs.

The Sr-concentration (right) is reduced in the activated regions surrounding the WEs (shaded), suggesting the oxygen vacancies ($V_O^{..}$) are consumed to form neutral lattice oxygen sites (O_O^x) when a cathodic potential is applied.



Electrode stability

60 nm (011) LSCF / (111) YSZ



The Ohmic resistance and ASR increase with time. Stability of Pt contacts affects R_{Ω} and active surface area for oxygen reduction.

Conclusions

- Due to the sheet resistance of thin films, the lateral electronic transport becomes comparable to the geometrically favored ionic transport perpendicular to the surface.
- The extent of activated surface area surrounding the WE is dependent on t_{ion} but not the applied potential.
 - $t_{ion}(LSM) < t_{ion}(LSCF)$
 - $dt_{ion}/dT > 0$
- Sputtered Pt-contacts are unstable at elevated temperature and are not suggested for long term experiments. Pressure contacts can provide stable contact.
- Extreme care should be taken when designing surface electrodes.
- The oxygen reduction and exchange reactions are not considered in this analysis

References

- M.E. Lynch & M. Liu, *J. Power Sources* **195**, 5155 (2010).
- N.J. Kidner, et al., *Thin Solid Films* **496**, 539 (2006); N.J. Kidner, et al., *Thin Solid Films*, **515**, 4588 (2007).

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