Role of Volatile Boron from Sealing Glass on Cathode Performance

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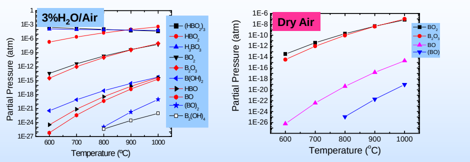
Research Background and Thermodynamic Calculations



High volatility of boron oxides (B_2O_3) at elevated temperatures in the presence of either air or fuel.

The most volatile species: **Boron hydroxides** (e.g HBO_2 and HBO_3) **in moist air**; **BO_2 in dry air**

Possible Reactions (Zhang et al. JAceS 2008)**:**

Formation of HBO_2 : $B_2O_3 + H_2O \rightarrow 2HBO_2(g)$ $\log(P_{HBO_2}) = 7.47 - 18972/T + 0.5\log p_{H_2O}$

Formation of H_3BO_3 : $B_2O_3 + 3H_2O \rightarrow 2H_3BO_3(g)$ $\log(P_{HBO_3}) = 0.41 + 463/T + 1.5\log p_{H_2O}$

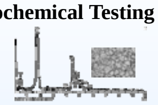
Formation of BO_2 : $B_2O_3(l) + \frac{1}{2}O_2 \rightarrow 2BO_2(g)$ $\log(p_{BO_2}) = 9.04 - 17406/T + 0.25\log(pO_2)$

Formation of B_2O_3 : $B_2O_3(l) \rightarrow B_2O_3(g)$ $\log(p_{B_2O_3}) = 13.89 - 20683/T$

Materials and Apparatus

1. Boron Sources and Electrochemical Testing

Boron Source: Glass: G59 (Sr 20%, Ba 20%, B 20%, and Si 40 wt%).



Test Fixtures: introduction of the boron sources without replacing the alumina tubes, with initial B-free baseline measurements.

2. Volatility Measurements

Volatilization: Flowing the selected gas (e.g., moisture air) across G59 glass located in the hot zone of a tube furnace.

Analysis: Glass condenser and water bubbler to catch boron species; ICP-mass spectrometry to measure concentration.

3. SIMS Analysis

Challenge: Boron is light, thus difficult to be probed with electron or x-ray spectroscopy; Very low concentration

SIMS: Secondary ion mass spectroscopy is sensitive to **light elements** (e.g. B) and **low concentration** (e.g. parts per billion)

Standards: boron standard samples for SIMS analysis made with a mixture of LSM-YSZ and sodium borates with boron concentration of 10, 100, and 1000 ppm.

Results and Discussion

1. Volatility Results

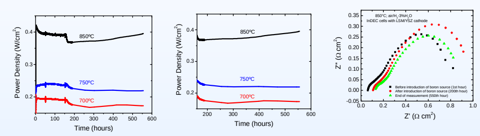
Volatility: The average boron transport rate from the glass in moist air (~3% water) was 3.2×10^{-12} g/cm^2-sec at 750ºC, which corresponds to a B species partial pressure of 1×10^{-9} atm, considerably lower than that theoretical values.

Discussion: The difference is likely due to: a) the lower activity of B in the glass compared to the B activity in B_2O_3, and b) the relatively high flow rate of air across the glass sample, which likely prevented saturation of volatile boron species in the air stream. Similar behavior is consistent with research of Cr volatility.

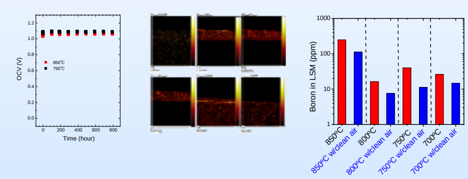
Material	T, ºC	Duration of test, h	Gas flow rate, cm/s	Average B transport rate, g/(cm^2-s)	Average B species partial pressure, atm
G59	750	300	5.1	3.2×10^{-12}	1.0×10^{-9}
G59	750	300	5.1	2.1×10^{-12}	6.6×10^{-10}

2. Effect of Boron on LSM

Electrochemical Performance: Immediate reduction in power density with introduction of boron; the performance then slightly increased with time. Impedance spectroscopy showed that introduction of boron resulted in higher electrode polarization.

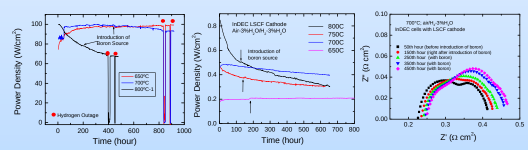


Discussion: OCV was stable, thus, the observed changes in cell performance were not caused by changes in the Nernstian driving force due to seal leaks, electrolyte cracks, etc. The performance reductions were at least partly a result of boron "poisoning". SIMS results indicate the presence of boron in the cathode. The boron concentration in the cathode was reduced if the boron source was removed. Volatile boron may physically absorbed on cathode surface without electrochemical interactions.

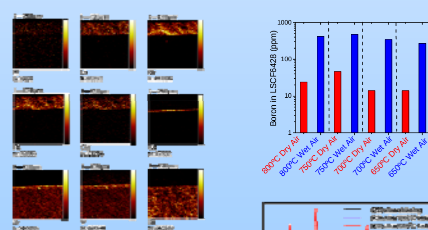


3. Effect of Boron on LSCF

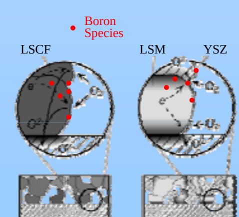
Electrochemical Performance: Absence of apparent changes of power density due to introduction of boron source in both dry and room-temperature moisture air at various temperatures. Both impedance and power density measurements indicate that volatile boron species did not cause immediate performance reduction.

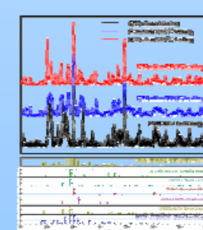


Discussion: SIMS results show that residual boron concentration in the cathode is much higher in moist air than in dry air. LSCF itself is a mixed ionic and electronic conductor; hence oxygen reduction occurs at the "double-phase boundary", which is the surface of LSCF particles in the cathode. Recent studies found that a substantial fraction of LSCF was inert during the electrochemical reactions.



Comparison between LSM-YSZ and LSCF: Volatile boron species were deposited on LSM/YSZ cathode surfaces, and effectively covered some fraction of triple phase boundaries of LSM/YSZ, thus reducing the power density. For LSCF, while volatile boron does cover some of the LSCF surface as shown in SIMS results, the effect is negligible due to a substantial fraction of available LSCF surface, which can become active and allow the cells to operate in the manner similar to the boron-free environment.





Phase evolution of boron glass after sintering and cell testing at various temperatures (700 and 850ºC)

Summary

- In agreement with thermodynamic calculations, boron oxide was confirmed to be volatile by both SIMS and volatility measurements.
- Volatile boron species can be incorporated into LSM, resulting in a decrease in power density. Boron species in LSM can be carried away from the cathode with clean air.
- Volatile boron species have negligible effect on the performance of LSCF. The difference in boron effects on LSM and LSCF cathodes is attributed to differing surface coverage by boron of active sites of the cathode, which effectively reduces triple phase boundaries in LSM/YSZ cathodes.

Acknowledgement

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