Development of Getters for Airborne Trace Contaminants Capture in SOFC Systems

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- Program objectives
- Program at glance
- Accomplishments
- List of publications
- Background
- Experimental
 - Getter synthesis, optimization and stability evaluation.
 - Validation of getter performance for co-capture.
 - Advanced anode materials synthesis and characterization. For Application in Stack
 - Validation using transpiration and electrochemical tests.
 - Posttest characterization
- Results and Discussion
- Future Work
- Acknowledgements







Program Objectives

- > The overall objective of the proposed research program is to:
 - develop cost effective approaches to mitigate cell and stack degradation as well as cost reduction via improvements in materials understanding.
 - > identify and validate cathode poisoning under "real world" air atmosphere.
 - Fabricate and test cost effective getter formulations and design to capture multi-components airborne impurities (Cr, S, Si and B) entering into SOFC power systems.
- Develop materials and architectures of cost-effective getters for application in stacks and BOP.
- Validate and demonstrate getter performance to capture trace levels of airborne multicomponents impurities.
- Identify other contaminants (intrinsic and extrinsic) originating from BOP and stack.
- Identify, synthesize and validate multi-constituent getter formulation for capturing Cr, S, Si and B impurities.
- Develop large scale getter synthesis process and validate under SOFC operating conditions.
- Technology transfer (industries or national labs)



Technical Challenge at a Glance

- Cathode remains the largest contributor of electrochemical performance degradation in SOFC
 - Cathode polarization losses (ohmic and non-ohmic)
 - Surface/interface compound formation.
- The long-term degradation is mostly irreversible as the chemical and morphological changes in the electrode is largely permanent.

Potential benefits of this project :

- The programs accelerate the commercialization of SOFC systems by improving the TRL.
- Mitigation of cathode poisoning and highly durable getters enables increased performance stability and long-term reliability of SOFC systems thus accelerating demonstration and deployment of the technology.



Outcome

- Mechanistic understanding of the degradation processes in pure electronic and MEIC cathodes.
- Development of mitigation process utilizing low cost getters to capture trace levels of airborne contaminants.
- Mechanistic understanding of cathode poisoning under "real world" air conditions
- Successfully developed, validated and implemented getters to capture Cr only, as well as Cr and S simultaneously.
- Identified extrinsic and intrinsic impurities from BOP and stack such as Cr, S, Si and B.
- Conducted materials and technology transfer.



Problem Statement

• Cathode poisoning in presence of airborne impurities, even in trace (ppm-ppb) level has shows rapid and irreversible degradations to cathode under high-temperature operating conditions.



This study remains significant and applicable to wide range of electrochemical technologies operating at high-temperature

Solid oxide fuel cells < solid oxide electrolysis cells < oxygen transport membranes < integrated gasification fuel cells

Power Gen < Hydrogen/fuel production < oxygen production < carbon capture technologies



Program Accomplishments

- > Cathode performance degradation has been studied under "real world" air atmosphere.
- Group-II alkaline earth and transition metal oxide based low cost getter efficiently captures trace airborne contaminants
- Getter performance has been validated for the capture of single (Cr or S) and multiple (Cr and S) contaminants in their trace concentrations in ppm-ppb range.
- > Electrochemical tests indicates stable cathode performance under SOFC systems conditions.
- Getter posttest characterization indicates high concentration of both Cr and S at the inlet, while no/negligible concentrations at the outlet indicating complete capture of contaminants.
- > Stability of advanced getter materials under ambient conditions has been evaluated.
- Presence of multi-contaminant (Cr, S, Si, B) is currently being investigated to understand their role on electrode poisoning
 - Graduate / Undergraduate students being trained 3
 - Post-doctoral fellows: 3
 - Outreach: Middle and High School, Davinci Program, STEM
 - Publications and presentations: Journal articles and technical society meetings



Intrinsic Impurities (NAAQS)

Gas	Concentration
Oxygen	20.9 v%
Nitrogen	78 v%
Water	<1 to 3 v%
Carbon dioxide	350 ppm
Sulfur dioxide	<1 ppm
Noble gases	<1 v%
Particulate matter (PM)	<50 μg/m³



Air in fuel cell stack and system may also contain component derived impurities such as Cr (from metals and alloys) and Si, B, and alkali (from glass and insulation).

Thermodynamic Calculations





Cathode Degradation in SOFC Systems

- Air electrodes remain prone to degradation due to acid-base interactions with contaminants
- Dopant exolution, Compound formation, Surface/Interface morphology changes and Interdiffusion



Trace Contaminant Getter: Concept





Figure. Schematic illustration of getter Integration within SOFC power system

- Cost-effective Strategy
 - May not need to do spinel-coating on all BoP components
 - No need to replace the established cathodes



Performance Evaluation: Sr-Ni-O



The electrochemical performance of LSM/YSZ half cell was maintained by using SNO-based getter.
The electrochemical performance of LSM/YSZ half cell was degraded under the flow of Cr vapor.



Performance Evaluation: Cr poisoning



STEM micrograph and EDS mapping on the cross section of the LSM electrode/YSZ electrolyte interface after the test in the presence of Cr vapor at 650 $^{\circ}$ C in 3%H₂O-air for 100 h.

► High Cr concentration at the LSM/YSZ interface

→ Electrochemical reduction reaction

TEM-diffraction patterns



TEM images of the chromium species deposited at the cathode interface taken along (a1) [110] and (b1) [011], HRTEM images of the crystallites (a2 and b2), the corresponding Fourier transform pattern of the same region as a2 and b2 respectively (a3 and b3), and the atomic model illustrated (a4 and b4).

- Electrochemical reduction
- : $2CrO_2(OH)_2(g) + 6e^- \rightarrow Cr_2O_3(s) + 2H_2O(g) + 3O^{2-}$
- ► Subsequent reaction of Cr2O3 with Mn in LSM \rightarrow (Mn,Cr)₃O₄



Cr Capture: SNO Mechanism



Illustration of chromium deposition on the LSM/LSZ interface (a) and the effect of the SNO getter mitigating the electrochemical degradation (b).



Advanced Getter Fabrication

SMO honeycomb getter by dip-coating



- Fabrication process of the SMO getter by dip-coating of a cordierite honeycomb substrate (400 cpsi) in an aqueous precursor slurry, followed by heat-treatment at 1000 °C,
- XRD patterns of a bare cordierite substrate and the SMO getter coated on the substrate
- SEM images of the inner channel and the surface of the SMO getter.

Honeycomb getters composed of $SrMnO_3$ has been fabricated by dip-coating of honeycomb cordierite substrate in $SrMnO_3$ aqueous slurry.



Performance Evaluation: Sr-Mn-O



Current density of the LSM|YSZ|Pt cells over time under the flow of either (a) 4 ppm SO₂ gas (injected after 110 h) or (b) Cr vapor toward the LSM cathode in the absence of SMO getter, and (c) that recorded under the flow of both Cr vapor and 4 ppm SO₂ gas (injected after 110 h) toward the LSM cathode through the SMO getter.

In the presence of SMO getter, the current remained stable validating the performance of the getter, whereas the current dropped under the flow of Cr vapor and SO_2 gas, individually.



Performance Evaluation: Sr-Mn-O

Electrochemical Test

- (a) S poisoning and (b) Cr poisoning
- Increase of Nyquist circles and Bode plots → Polarization resistance increase due to reactions of Cr and S with LSM
- (c) Cr/SO₂ with getter
- Static Nyquist circles and Bode plots
- Relatively clean morphology of both LSM surface and LSM/YSZ interface
- \rightarrow S/Cr gases were captured by the SMO getter



Impedance spectra (Nyquist and Bode plots) of the LSM|YSZ|Pt cell under the conditions 1–3 (Table 1), and cross-sectional SEM images at the LSM/YSZ interface exposed to (a) SO2 gas, (b) Cr vapor, and (c) both Cr vapor and SO2 gas in the presence of the SMO getter, respectively.



Thermal and Hydrolytic Stability: Sr-Mn-O



High-temperature XRD patterns of $SrMnO_3$ powder: room temperature (RT), 500 °C, 700 °C, 900 °C, and RT after cooling down.

No structural change of $SrMnO_3$ at high temperatures (up to ~1400 °C)



XRD patterns of (a) as-synthesized SrMnO₃ powder, (b) the power placed in a humid environment (2.7% H_2O) for 2 weeks, and (c) the powder soaked in water for a day; and (d) Photographs of SrMnO₃ pellets before and after exposure to the humid environment for 12 days.

No structural change of SrMnO₃ in humid environment.



Capture Mechanism: Sr-Mn-O

(a) XPS depth profile of a SrMnO₃ pellet that was heat-treated at 700 °C for 100 h in ambient air, (b–e) Montage of depth profile survey spectra for Mn, Sr, O, and C, and (f) Raman spectrum of the SrMnO₃ surface.



Thermodynamic Calculations: Stability



Phase diagram as functions of the partial pressure of $SO_{2(g)}$ and temperature for the reaction between $SrCrO_4$ and $SO_{2(g)}$. Phase diagram for Mn_2O_3 - Cr_2O_3 system (ss: solid solution; Tetr.: tetragonal; L: liquid). Modified in part with permission from Ref. [W. Qu et al., *Journal of Power Sources* 153, no. 1 (2006): 114-124.].



Chromium and Sulfur Combined Poisoning





Figure (a) Current densities and (b and c) Impedance spectra of LSM|YSZ|Pt and LSCF|GDC|Pt solid oxide cells recorded over time (up to 110 h) at 750 °C under the flow of 500 ppb $SO_{2(g)}$ and Cr vapor (~1 ppb $CrO_2(OH)_{2(g)}$) toward the LSM and LSCF air-electrodes. (d) Their ohmic and non-ohmic resistance change over time.

LSM: Rapid degradation due to polarization resistance increase

► LSCF: Slower degradation due to both polarization and ohmic resistance increases



Thermodynamic: Cr&S Capture



Phase stability diagram for a fixed SrO and varying partial pressures of SO₂ and $CrO_2(OH)_2$ at 750 °C. The red spot indicates the partial pressures of the chromium and sulfur species in this work.

- ► The feasibility of the reaction between SrO (surface-segregated on LSCF) and Cr/S impurities and the compounds were figured out.
- ► The thermodynamic analysis validates that the reaction behavior related to Cr/S contamination is affected by the partial pressures of Cr and S species.
- ▶ In this experimental condition, the reactivity of SrO with SO_2 was higher than that with Cr vapors.



Chrome and Sulfur Combined Poisoning



(a) Schematic of the cross-sectional structures of LSM and LSCF contaminated with Cr and/or S species, drawn from Table 1. The combined Cr and S poisoning behavior of LSM is equivalent to the sum of those of individual Cr and S poisonings. However, the combined Cr and S poisoning behavior of LSCF is different from the sum of those of individual Cr and S poisonings. (b) The expected process of the combined Cr and S poisoning in LSCF.

► Adsorption/absorption of SO_{2 (g)} onto the Sr-enriched LSCF and segregated SrO

Cr vapor penetrating into the electrolyte without being absorbed by LSCF, since pre-adsorbed SO₂ has already deactivated the Cr-gettering effect of LSCF.



Interactions of multiple contaminants in SOFC systems



Contaminants presence in air and the ones that evaporates from BOP and IC leads to poisoning



Multi-Contaminant Getter validation techniques

Transpiration tests



Response parameters:

- Contaminants vapor pressure
- Getter validations
- Posttest getter morphology and chemistry
- Cathode performance: surface and cross section







Borosilicate Glass in High Temperature



Comparison of glass beads (a-h) before and (e-h) after exposure to humid air at 750 °C for 300 h. (a) and (e) show the photograph of the glass beads before and after the treatment. (b-d) and (f-h) show the SEM images of the before and after treated glass bead surface. Higher magnification is shown from left to right.

► Borosilicate beads still maintain their morphology after heat-treatment at 750 °C



Borosilicate Glass at High Temperature



Figure. XRD patterns of the glass beads before (black spectrum) and after (blue spectrum) the 300 h test in humidified air.

Figure. (a) XRD pattern of a borosilicate glass used for the experiment, and (b) Weight change of the borosilicate glass with time.

► At high temperatures, borosilicate is crystallized into SiO_2 cristobalite while the weight decreases due to Si/B vapor generation.



B/Si poisoning of LSM electrode

Electrochemical performance of the LSM/YSZ/Pt cell at 700 °C for 100 h under the flow of humidified air (3% H_2O -air) in the presence of borosilicate. (a) Current density plot, and (b) corresponding Nyquist plots recorded after 1, 4, and 55 hours.



The LSM performance (current density and polarization resistance) decreases over time in the presence of borosilicate glass beads.



B/Si poisoning of LSM electrode



SEM image of the LSM exposed to Si and B species for 100 h during the EIS test, and EDS spectra of selected regions from the LSM surface to the LSM/YSZ interface.

Post-test characterization of LSM exposed to Si/B vapors indicates the presence of boron. However, the signal for B in EDS is too small to be quantified. Si was not detected by EDS analysis.



B/Si poisoning of LSM electrode



▶ B and Si concentrations in Na_2CO_3 absorbent in the absence (0-300 h) and presence (300-600 h) of borosilicate have been analyzed by ICP.

► The boron concentration in Na_2CO_3 decreased, indicating the absorption of boron vapors onto SMO getter and/or the decrease in B vaporization from borosilicate.



Conclusions

- > Cathode poisoning mechanism have been developed under extrinsic and intrinsic impurities.
- Thermodynamic calculations indicate significant vapor pressure of impurities at elevated temperature and humidification levels.
- > Mitigation of cathode poisoning have been demonstrated using alkaline oxide materials.
- > Capture of single (Cr only) and dual (Cr and S) contaminants have been successfully demonstrated.
- > Hydrolytic phase stability of getter materials as a function of temperature has been investigated.
- > Variety of getters have been synthesized and testes: Sr-Ni-Ox, Sr-Fe-Ox and Sr-Mn-Ox.
- > Large scale SMO getter have been synthesized (200g)
- > Advanced coating with uniform thickness and morphology has been obtained on cordierite substrate.
- **Gas phase multi-impurities (Cr, S, Si, B) exists in high-temperature SOFC operating conditions.**
- > Thermodynamic analysis show a number of getters which can capture these impurities.
- > SMO getter has been shipped to Alfred University for developing novel coating techniques.



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Thank You

