Capture of Trace Airborne Impurities and Mitigation of Electrode Poisoning in SOFC

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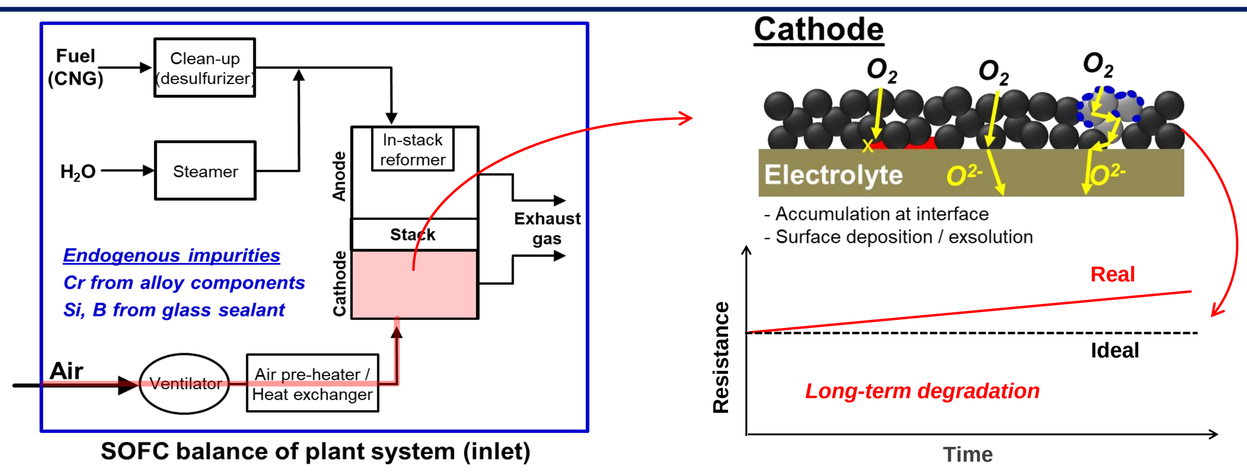
Executive Summary: Trace levels (from ppm to sub-ppb) of intrinsic and extrinsic gas phase impurities, present in the oxidant air stream entering the SOFC power generation systems, lead to electrode poisoning and irreversible electrochemical performance degradation during long term operation. The gaseous impurities have tendency to accumulate, react, poison the electrochemical sites and contribute towards an increase in both ohmic and non-ohmic electrode polarizations. A novel "Getter" approach for the capture of gaseous contaminants from the air stream has been developed to prevent electrode poisoning. Oxides consisting of alkaline earth and transition metals have shown a superior performance for capturing Cr and S contaminants. Experimental details pertaining to the fabrication of a robust getter capable of capturing both Cr and S gaseous species will be discussed. Time-resolved electrochemical impedance spectroscopy and I-t curves have demonstrated superior getter performance and electrode stability during benchtop experiments using air streams containing Cr and S impurities. Parameters influencing the structural stability of the getter will be presented.

Technical Background:

Cathode poisoning by airborne contaminants remains a primary cause of the performance degradation of SOFC power systems in long-term. While a trace level (~75 ppb) of SO_2 remains airborne, the significant evaporation of Cr vapors ($CrO_2(OH)_2$ and CrO_3) occurs in the presence of humidified air from chromia scale which is formed to passivate the metallic components (interconnect and balance-of-plant) from further oxidation and corrosion. The interaction of these contaminants with cathode materials results in the formation of secondary compounds and the retardation of oxygen reduction reaction (ORR). Advanced getter composition and validation tests have been presented to demonstrate combined capture of Cr and S impurities to mitigate the cathode poisoning.



Scheme 1. The mechanism of cathode performance degradation by gaseous impurity contamination in SOFC-BoP systems

Experimental

Techniques ➡ Electrochemical and Plug Flow Reactor Tests

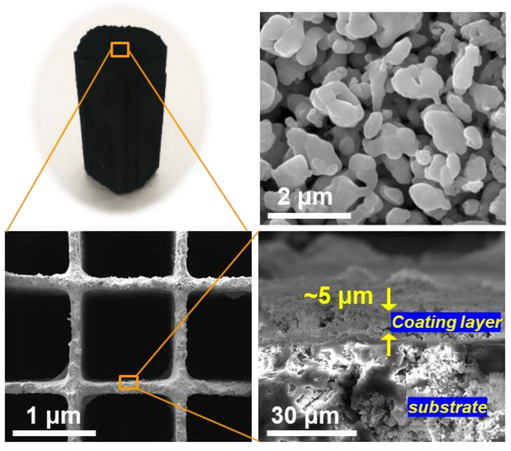


Figure 1. Photo and SEM images of Cr and S co-getter

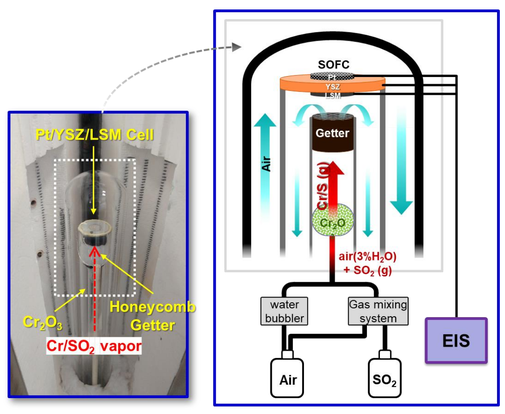
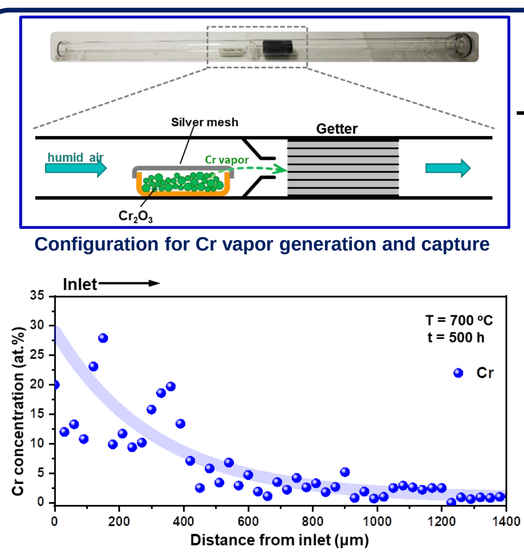


Figure 2. Configuration for the electrochemical impedance spectroscopy (EIS) measurement on LSM‖YSZ‖Pt cells under the flow of Cr and S gaseous species through the honeycomb getter.

Parameters

Temp	500-900 °C
SO_2	0.5-4 ppm
Cr vapor	~1ppb
Exposure	Humid Air
Time	100-1000 hrs.
Getters	Honeycomb



Configuration for Cr vapor generation and capture

Figure 7. Distribution of Cr along the inner channel of the getter, analyzed using EDS.

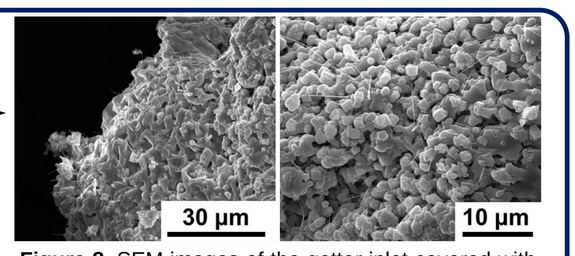


Figure 8. SEM images of the getter inlet covered with nanowhiskers.

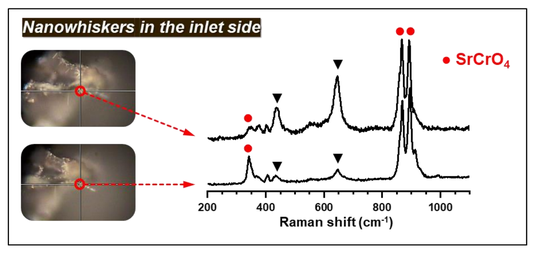


Figure 9. Raman spectra of the nanowhiskers grown on the inlet.

Results

Electrochemical Performance

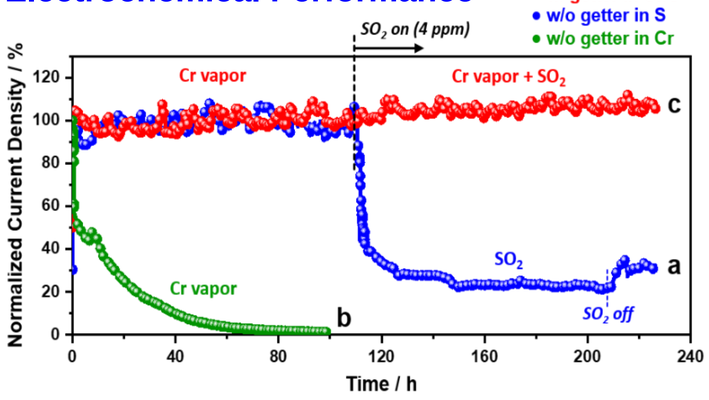


Figure 3. I-t curves of LSM‖YSZ‖Pt cells under the flow of (a) 4 ppm SO_2(g) (feeding after 110 h) and (b) chromium vapor (~1 ppb) onto the LSM cathode in the absence of getter, and (c) that under the flow of both chromium vapor and 4 ppm SO_2(g) (feeding after 110 h) in the presence of the getter.

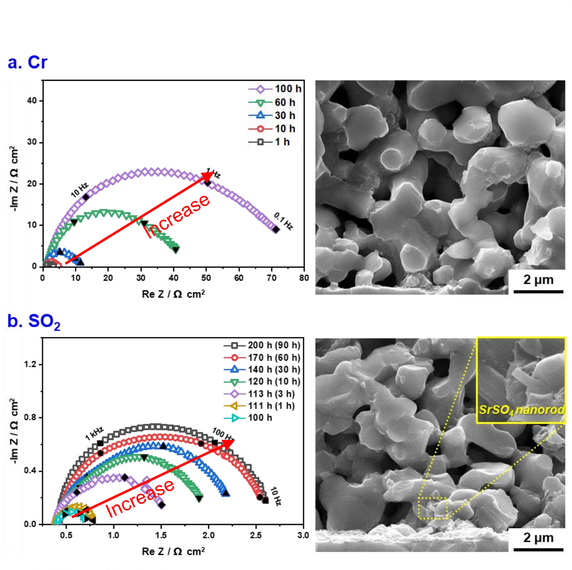


Figure 4. Nyquist curves from the LSM‖YSZ‖Pt cell under the SO_2 gas and Cr vapor, and cross-sectional SEM images at the LSM/YSZ interface exposed to (a) Cr vapor, (b) SO_2 gas, and (c) both Cr vapor and SO_2 gas in the presence of the getter, respectively.

Cr and S Capture Trend

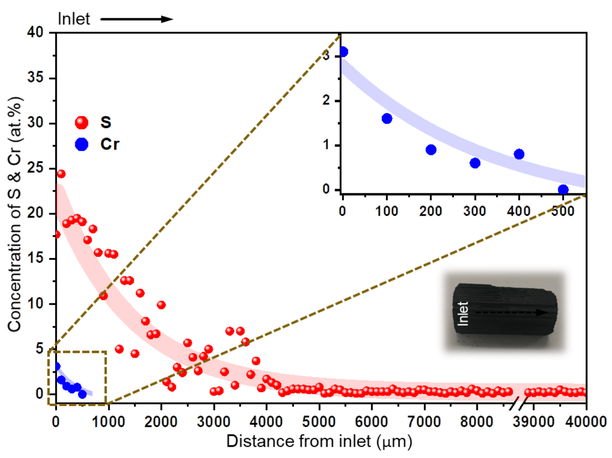


Figure 5. Distribution of S and Cr along the inner channel from the inlet to the outlet of the getter that was exposed to 4 ppm SO_2 (120 h) and ~1 ppb Cr vapor (230 h) at 700 °C, analyzed using EDS.

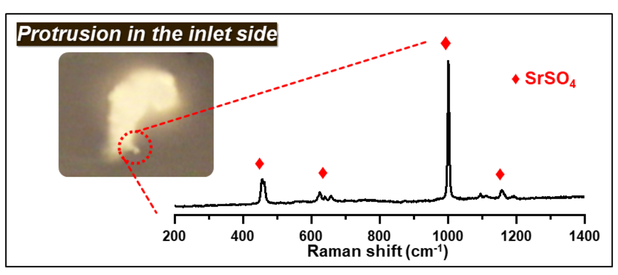
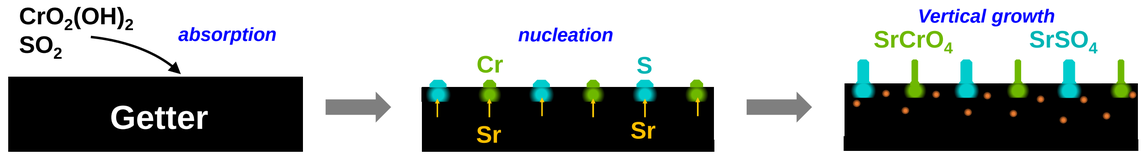


Figure 6. Raman spectrum of the nanorod grown on the inlet of the getter.

Discussion:

Experimental results demonstrate the viability of the getter for capturing airborne Cr and S contaminants.

- The getter's capability for capturing Cr and S contaminants is evaluated using EIS tests.
- The electrochemical performance of the LSM‖YSZ‖Pt cell is maintained in the presence of the getter under the air flow containing Cr and S impurities, whereas the performance is degraded in the absence of the getter.
- Raman spectra show that the absorption of Cr and S species onto the getter leads to the formation of $SrCrO_4$ and $SrSO_4$, respectively.
- SEM observation shows that the absorption reaction is accompanied by the morphological elongation such as the growth of nanorods/whiskers, which favors the continued absorption.



Scheme 2. S and Cr capturing process accompanied by morphological elongation

Research Impact

- The process is applicable to high temperature electrochemical systems
- Process can be effectively used for space and terrestrial systems.
- A cost-effective method to mitigate long-term cathode poisoning in SOFC

Illustration of Cr/S honeycomb getter to purify the Cr and S contaminated airstream

Publications

- Hong, J., Heo, S.J., Aphale, A.N., Hu, B. and Singh, P., *Journal of The Electrochemical Society*, 166(2), pp.F59-F65. 2019
- Aphale, A., Hu, B. and Singh, P., *Journal Of Metals*, 71(1), pp.124-130, 2019
- Aphale, A., Uddin, M.A., Hu, B., Heo, S.J., Hong, J. and Singh, P., *Journal of The Electrochemical Society*, 165(9), pp.F635-F640, 2018
- Liang, C., Hu, B., Aphale, A., Venkataraman, M., Mahapatra, M.K. and Singh, P., *ECS Transactions*, 75(28), pp.57-64, 2017

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