Mitigation of Chromia-poisoning in Solid Oxide Fuel Cell Cathodes

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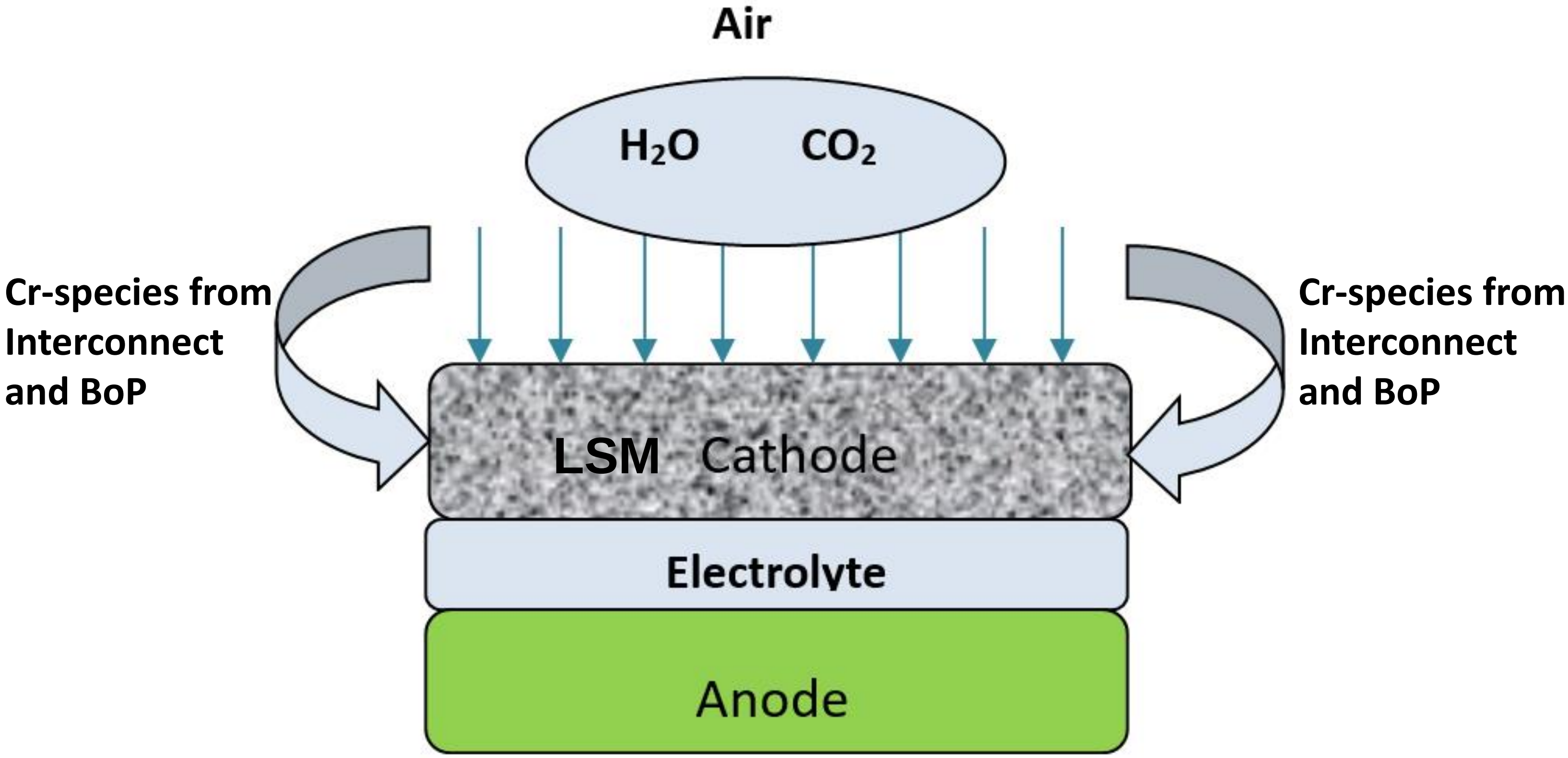
south carolina solid oxide fuel cells
CENTER OF EXCELLENCE

UNIVERSITY OF SOUTH CAROLINA
DEPARTMENT OF MECHANICAL ENGINEERING

Outline

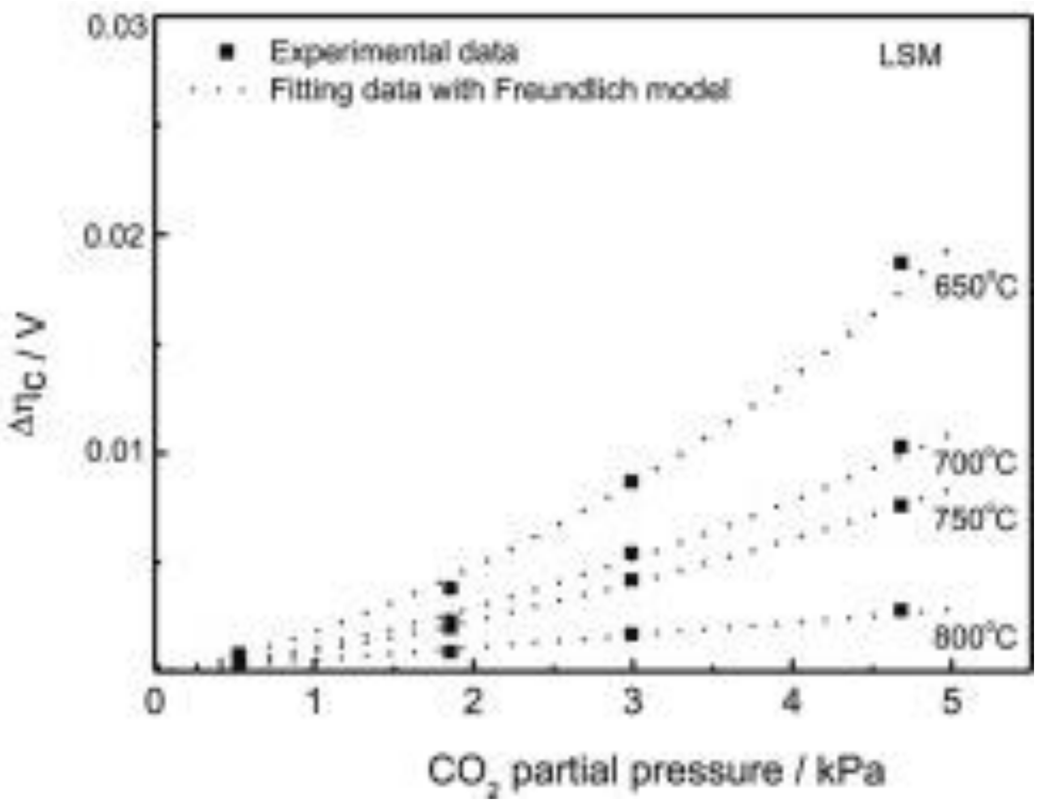
- **Background**
- **Project objectives and work progress**
  - **Alternative $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) cathode**
  - **$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) as Cr-getter**
  - **Coating to mitigate Cr-poisoning**
- **Summary**

Background – Cathode Degradation due to the Environment



Schematic illustration of the possible cause of performance degradation of the LSM cathode materials

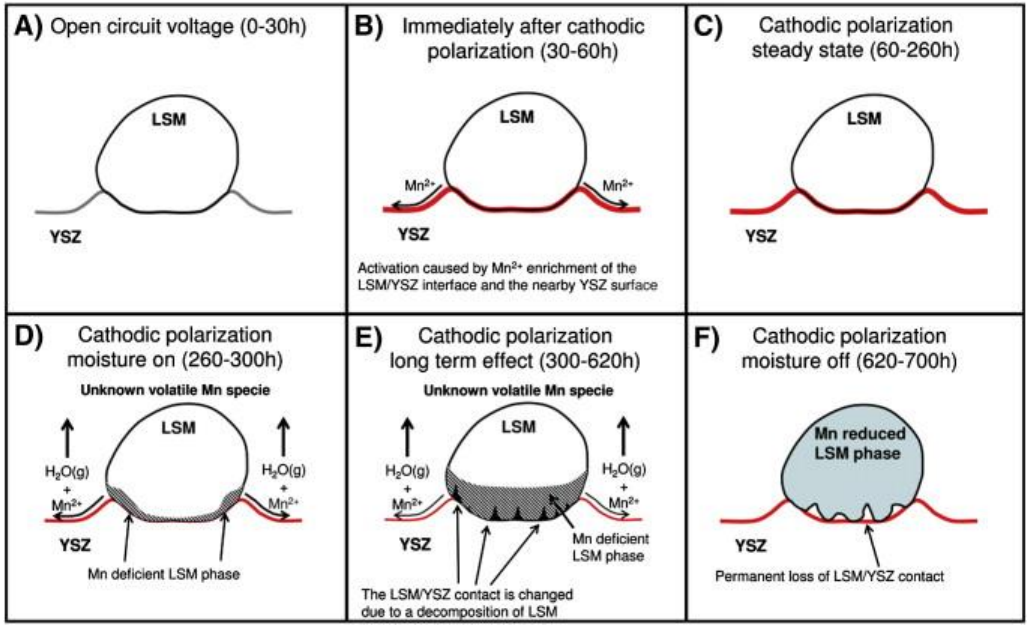
CO_2 Impact on LSM Cathode Durability



The effects of carbon dioxide on oxygen reduction reactions on LSM cathodes: CO_2 inhibits dissociation of adsorbed oxygen molecule or diffusion of O-species on the LSM cathode

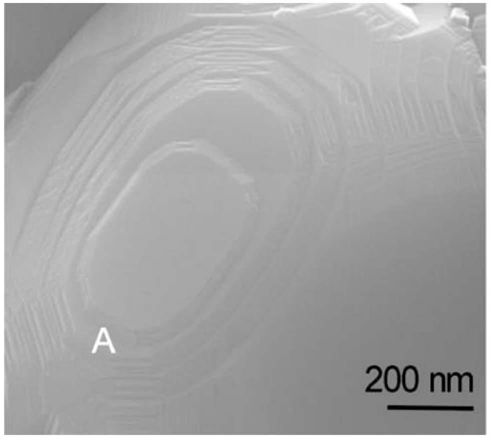
J. Power Sources 2013, 222, 542-553

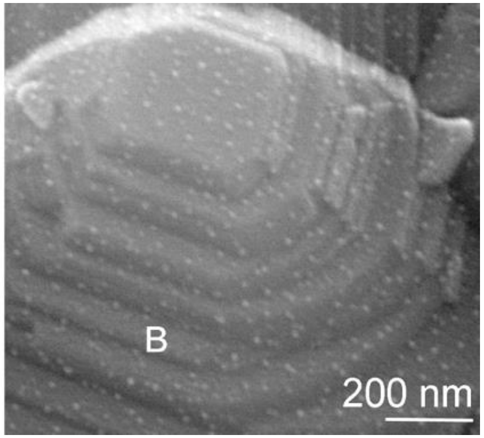
Instability of LSM under Moisture



Moisture causes an enhanced removal of manganese from the LSM/YSZ interface and thus eventually a decomposition of LSM

Solid State Ionics 2011, 189, 74-81



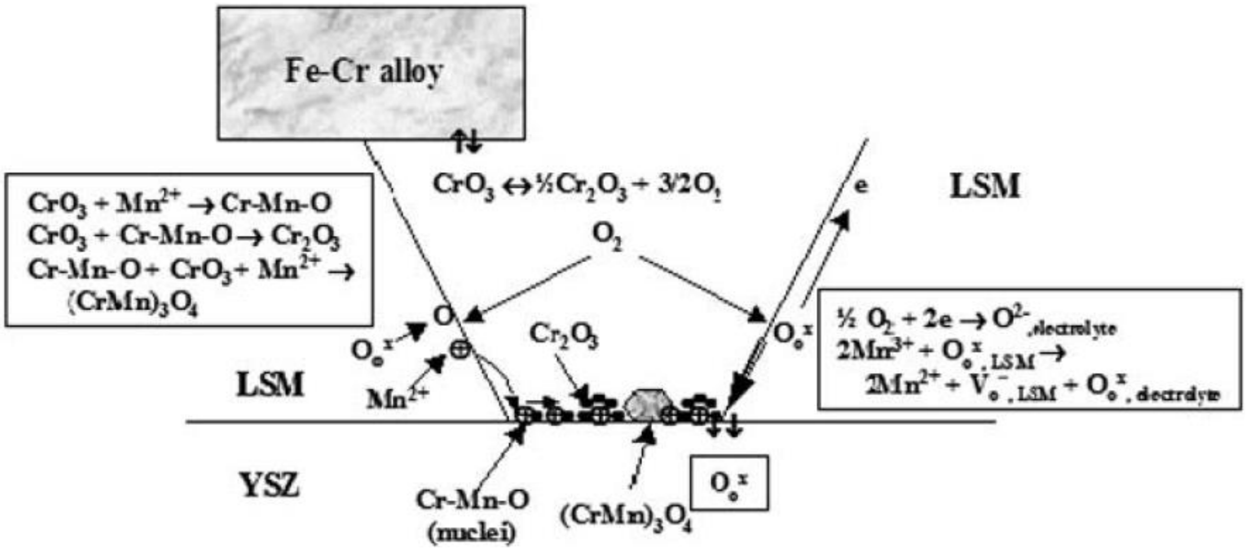


H_2O effect (LSM in dry air and 3% H_2O air)

Formation of $Sr(OH)_2$ on LSM surface

Journal of the Ceramic Society of Japan 2015, 123, 199-204

Cr Poisoning – Chemical Pathway



Mn^{2+} serves as nucleation agent for the formation of Cr_2O_3 from Cr-Mn-O nucleus

$Cr_2O_3(s) + 3/2O_2 \rightarrow 2CrO_3(g)$ (1)

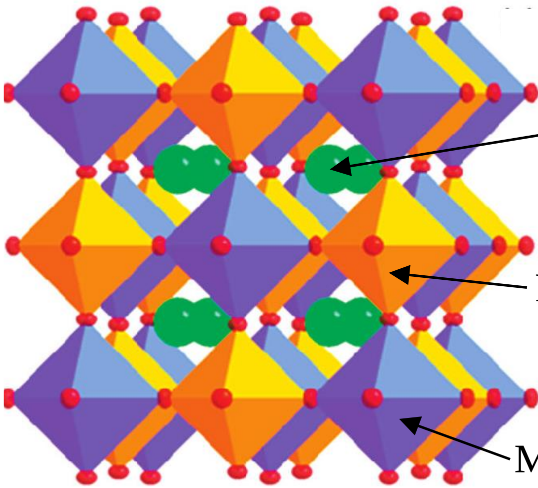
$Mn^{2+} + CrO_3 \rightarrow Cr–Mn–O_x$ (nuclei) (2)

$Cr–Mn–O_x$ (nuclei) + $CrO_3 \rightarrow Cr_2O_3$ (3)

$Cr–Mn–O_x$ (nuclei) + $CrO_3 + Mn^{2+} \rightarrow (Cr,Mn)_3O_4$ (4)

J. Mater. Res. 2005, 20, 747-758

Alternative Cathode – $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM)



Composition	σ_i (Scm^{-1}, 800C)
SFM	0.13
$La_{0.8}Sr_{0.2}MnO_3$	5.93×10^{-7}
$La_{0.6}Sr_{0.4}CoO_3$	0.22
$La_{0.8}Sr_{0.2}Co_{0.8}Fe_{0.2}O_3$	0.04

- Sr_2FeMoO_6 -> **presence of Fe^{2+}/Fe^{3+} and Mo^{5+}/Mo^{6+}**
- $Sr_2Fe_{1.5}Mo_{0.5}O_6$ -> **Fe^{3+}/Fe^{4+} and Mo^{5+}/Mo^{6+}**

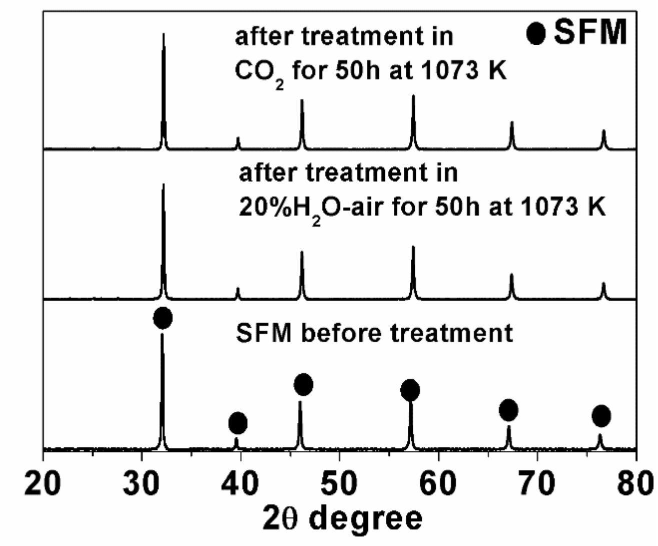
Fe-O-Fe	Sr_2FeMoO_6	$Sr_2Fe_{1.5}Mo_{0.5}O_6$
$E_{f,vac}$ (eV)	~3.1	~0.85 (max 1.09 - min 0.45)

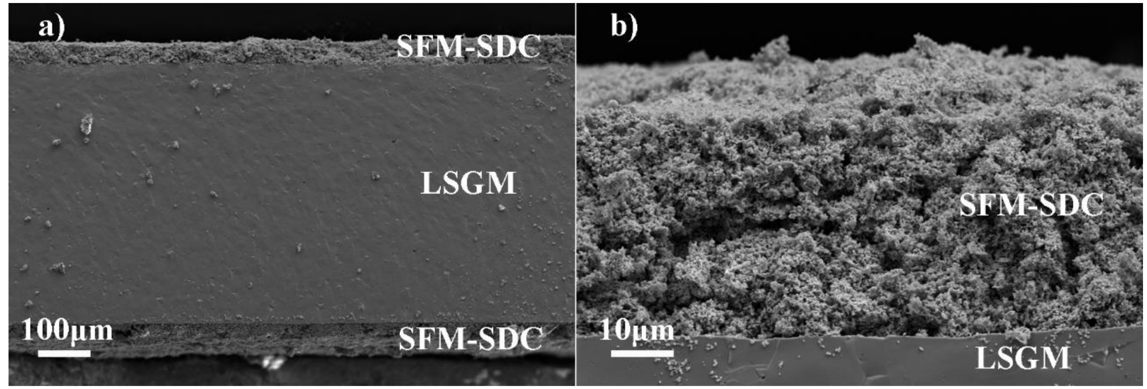
Eliminate $V_O^{\bullet\bullet}$ - Sr'_{La}

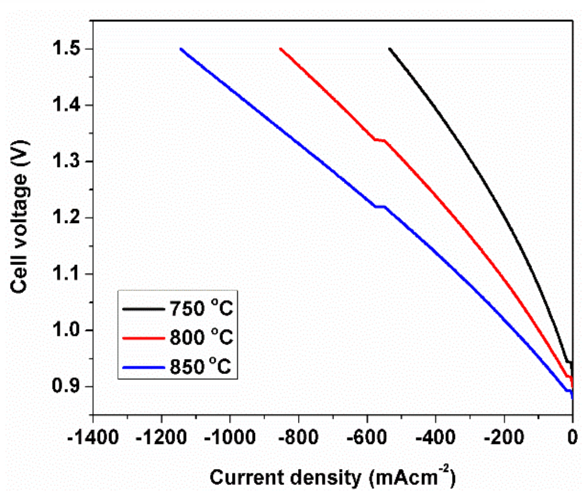
Mn-free composition

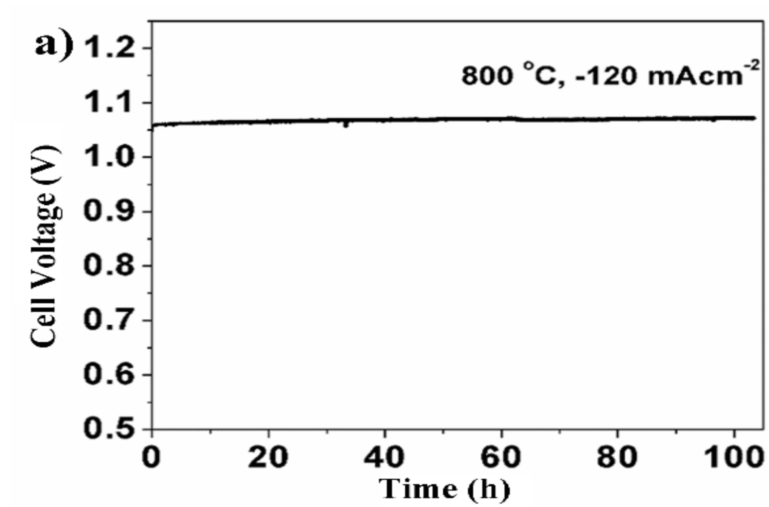
Advanced Materials, 2010, 22, 5478-5482
Journal of the Electrochemical Society, 2011, 158, B455-B460

SFM Stability in Moisture and CO_2





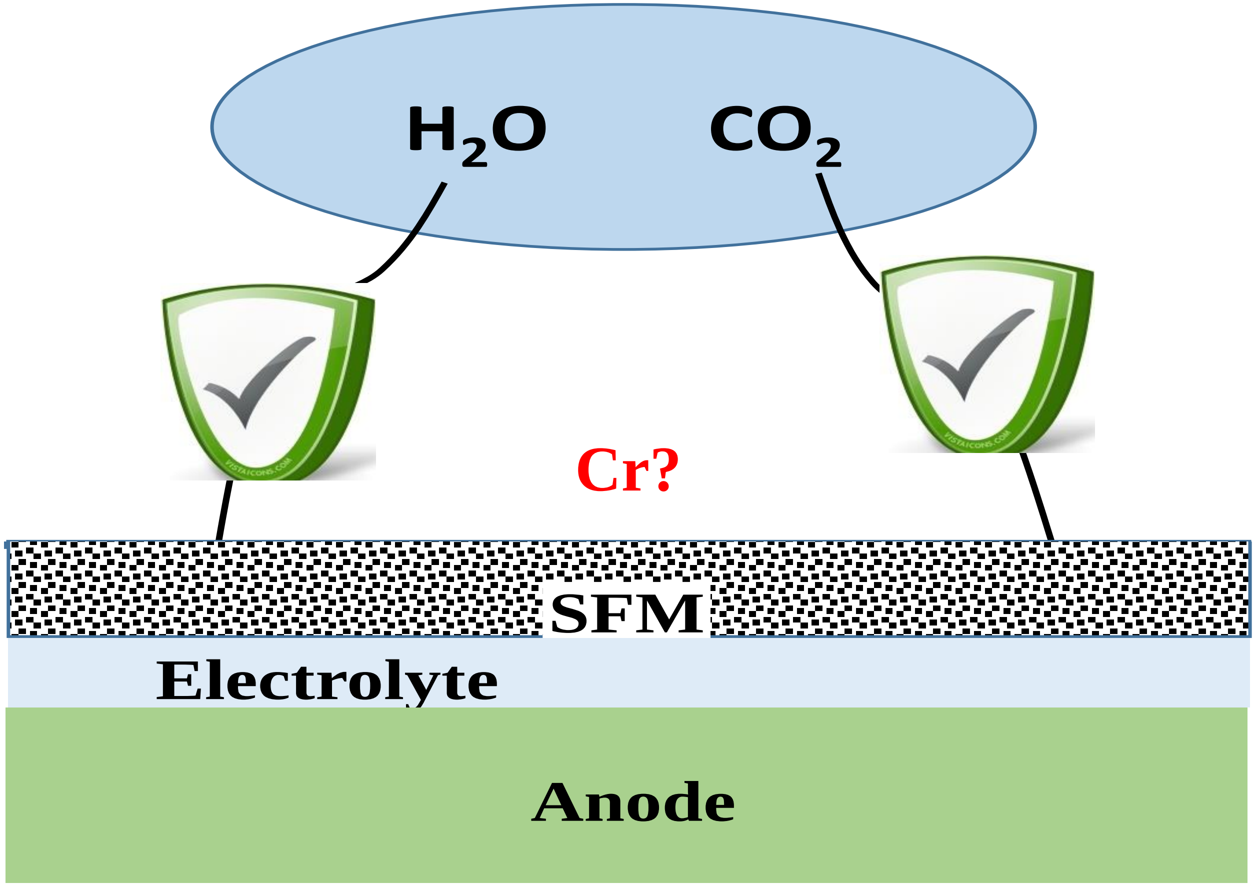




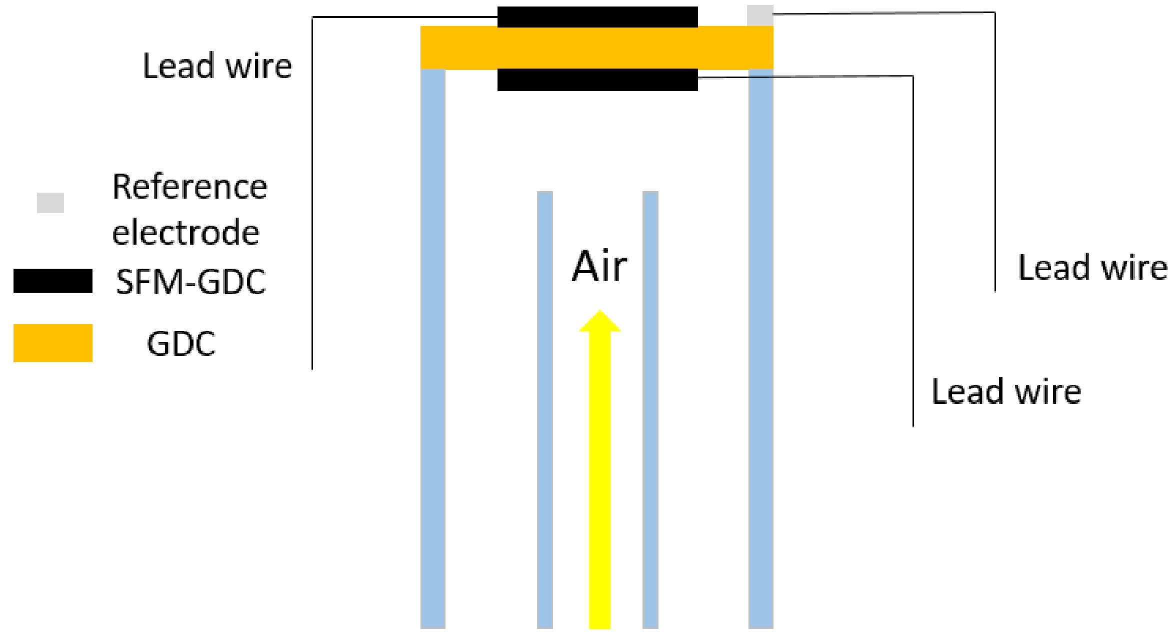
Stable cell performance of symmetrical cell SFM-SDC/LSGM/SFM-SDC under co-electrolysis operation.

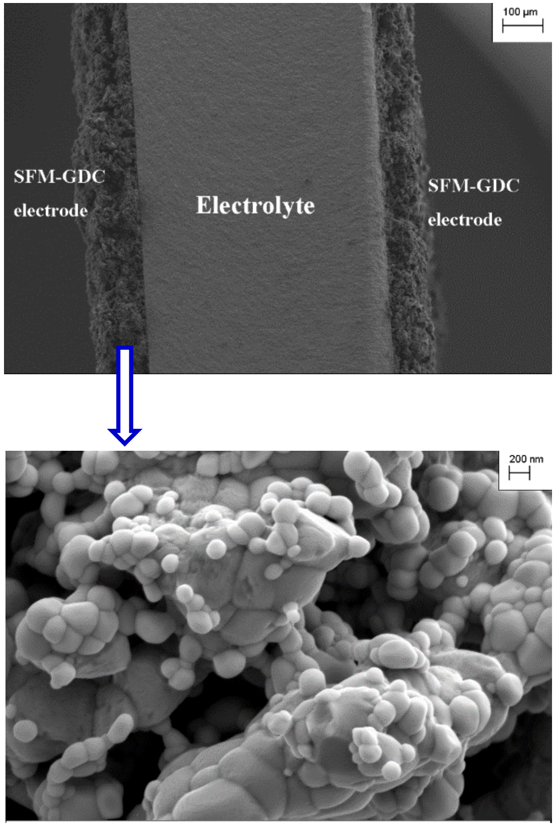
J. Power Sources 2016, *305*, 240-248

Project Objective 1 – Cr-tolerant Cathode?



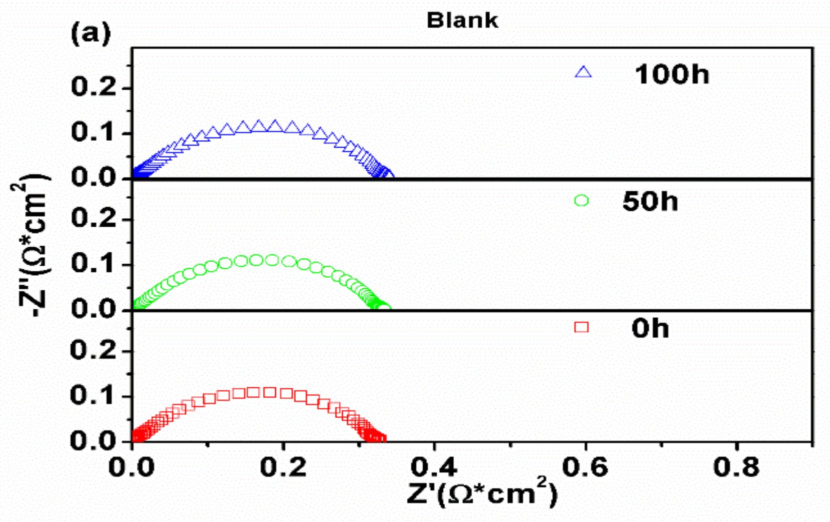
Half-cell Evaluation of Pristine SFM Cathode

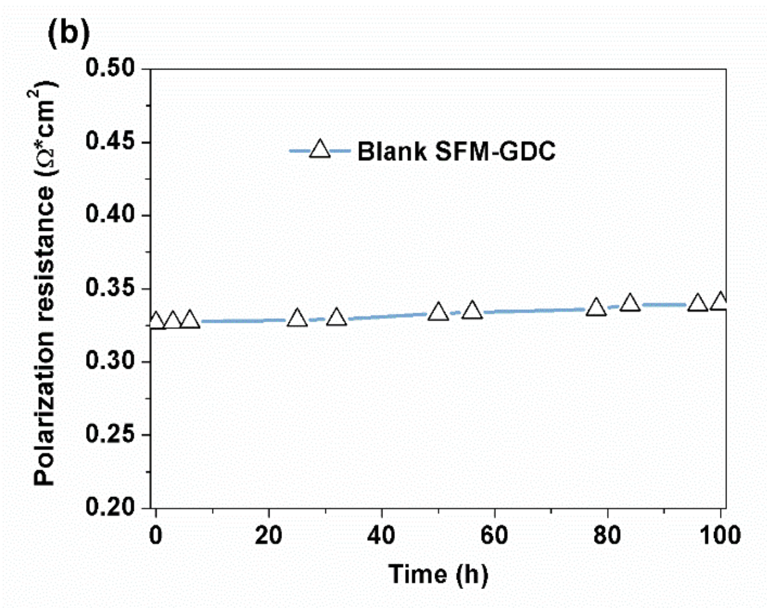


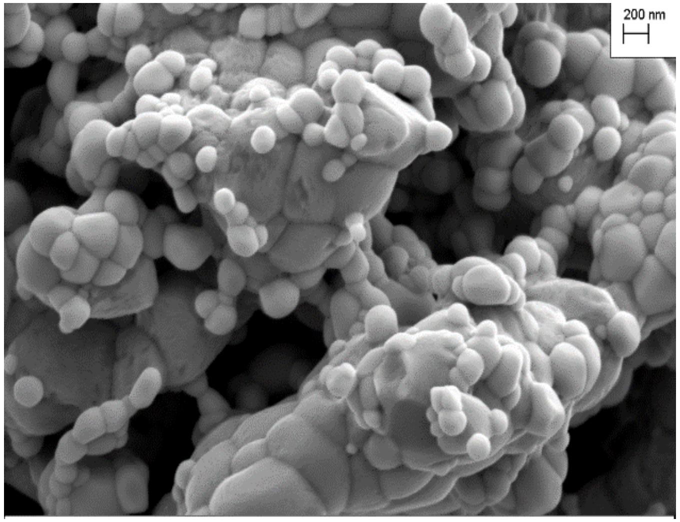


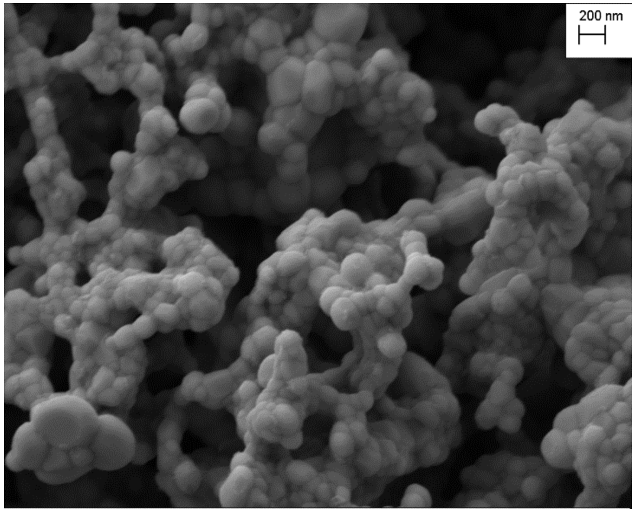
- Symmetrical half-cells of SFM-GDC electrodes on both sides of the GDC electrolyte.
- The electrolyte layer is dense, while the SFM-GDC electrode is porous.

Half-cell Evaluation of Pristine SFM Cathode



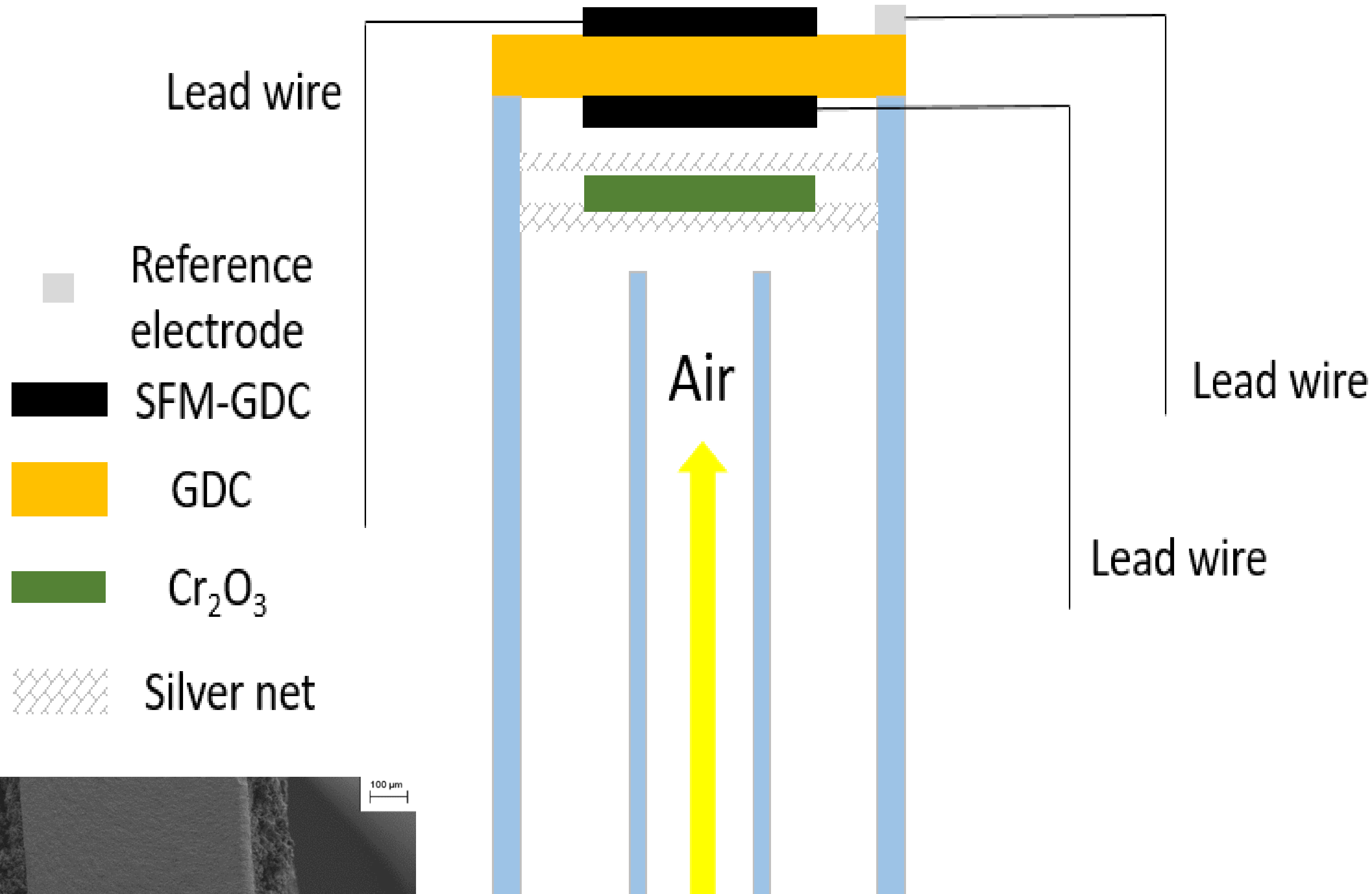


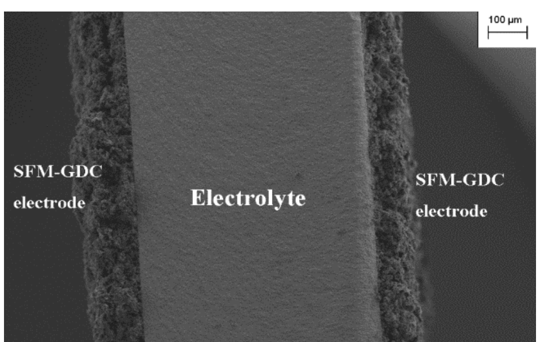




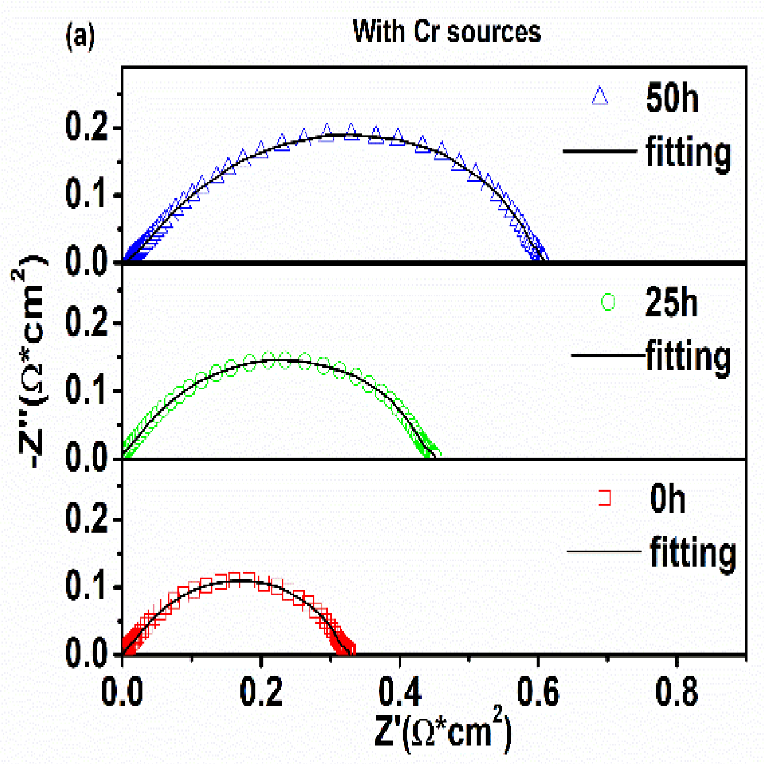
before (left) and after short-term test (100 h) at 1073K.

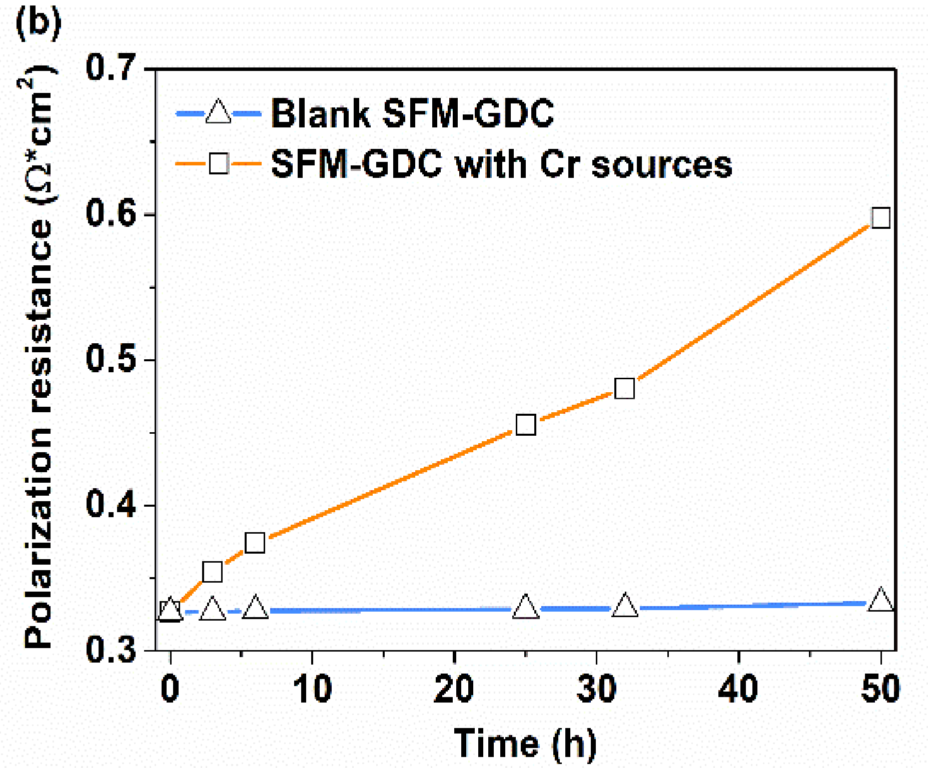
Cr-tolerance Test of SFM Cathode

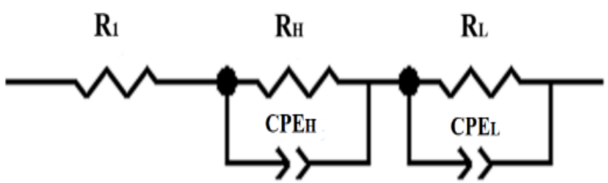


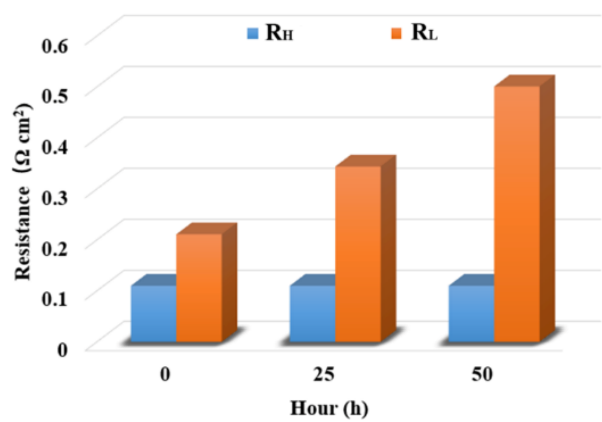


SFM Cathode Performance under Cr-containing Environment



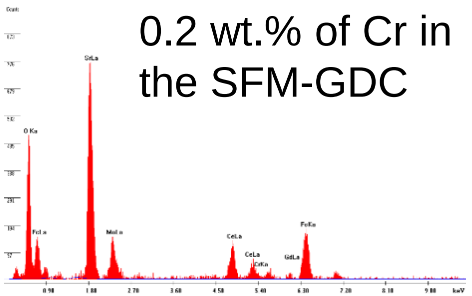




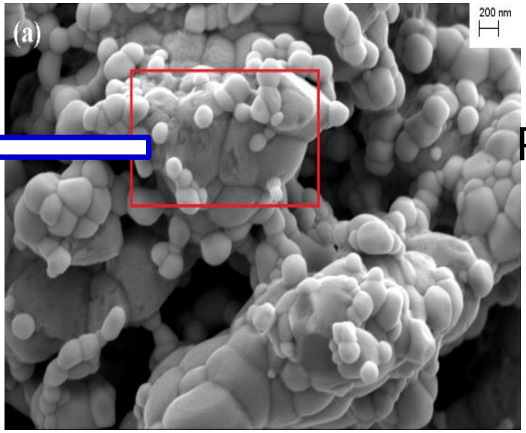


SFM Cathode w/ and w/o Cr-Contaminants

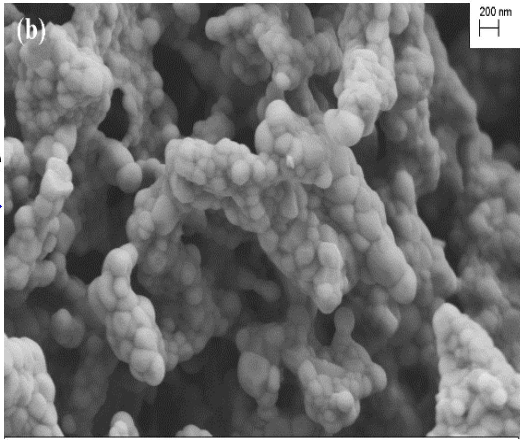
Due to partial overlap of Ce and Cr peaks



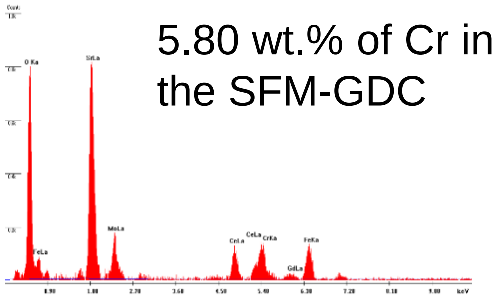
0.2 wt.% of Cr in the SFM-GDC



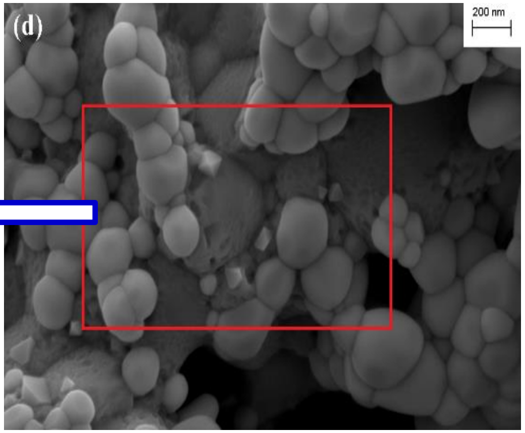
Pristine

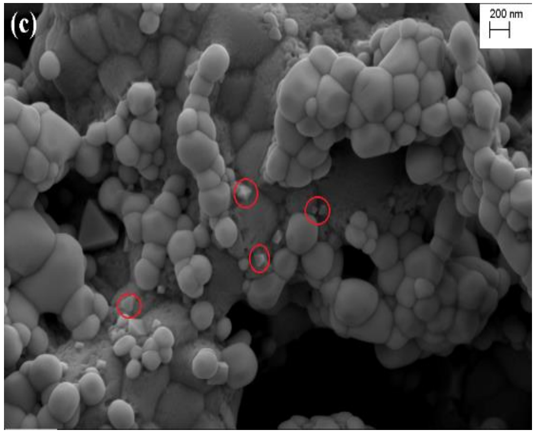


With Cr-contaminants



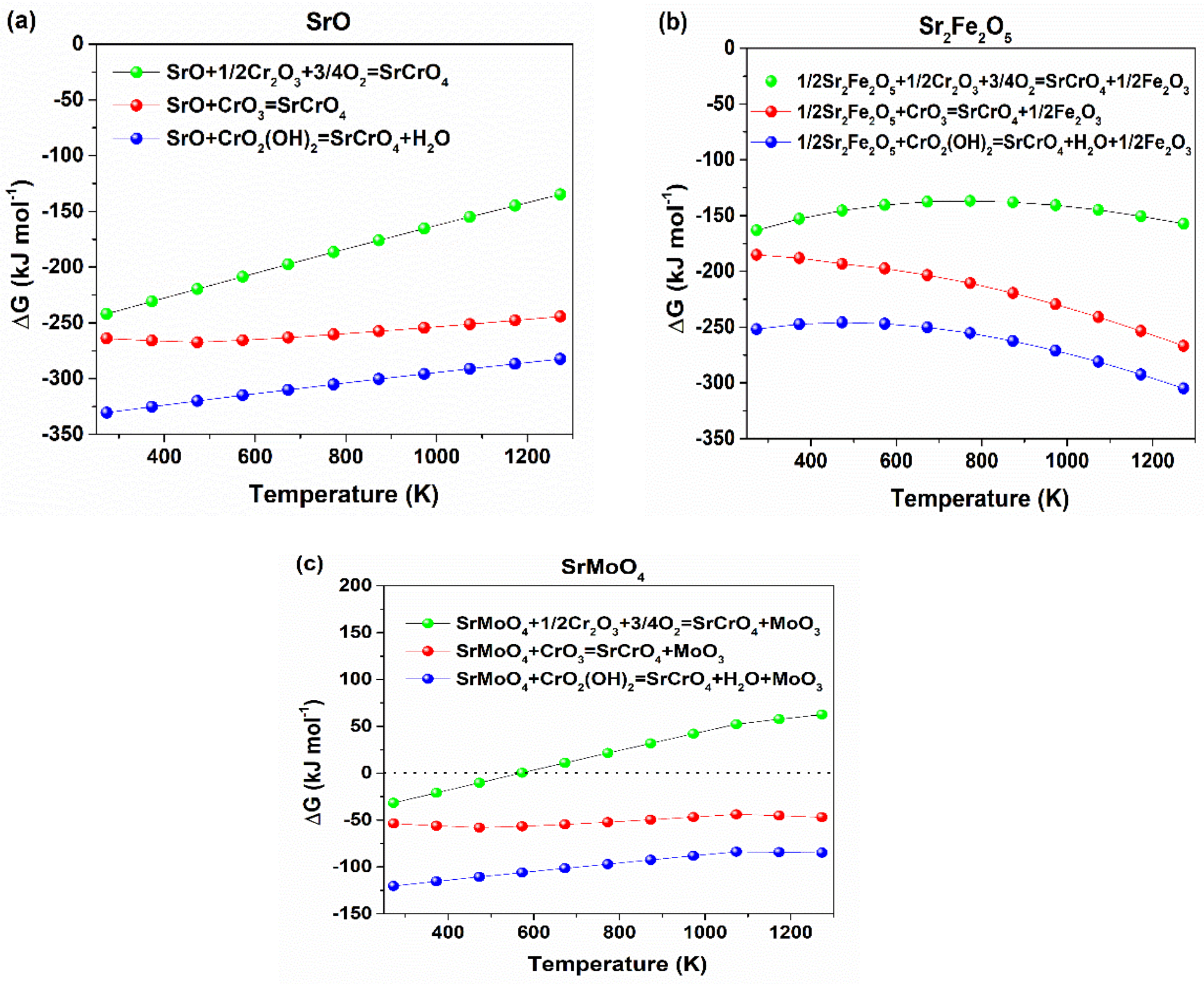
5.80 wt.% of Cr in the SFM-GDC



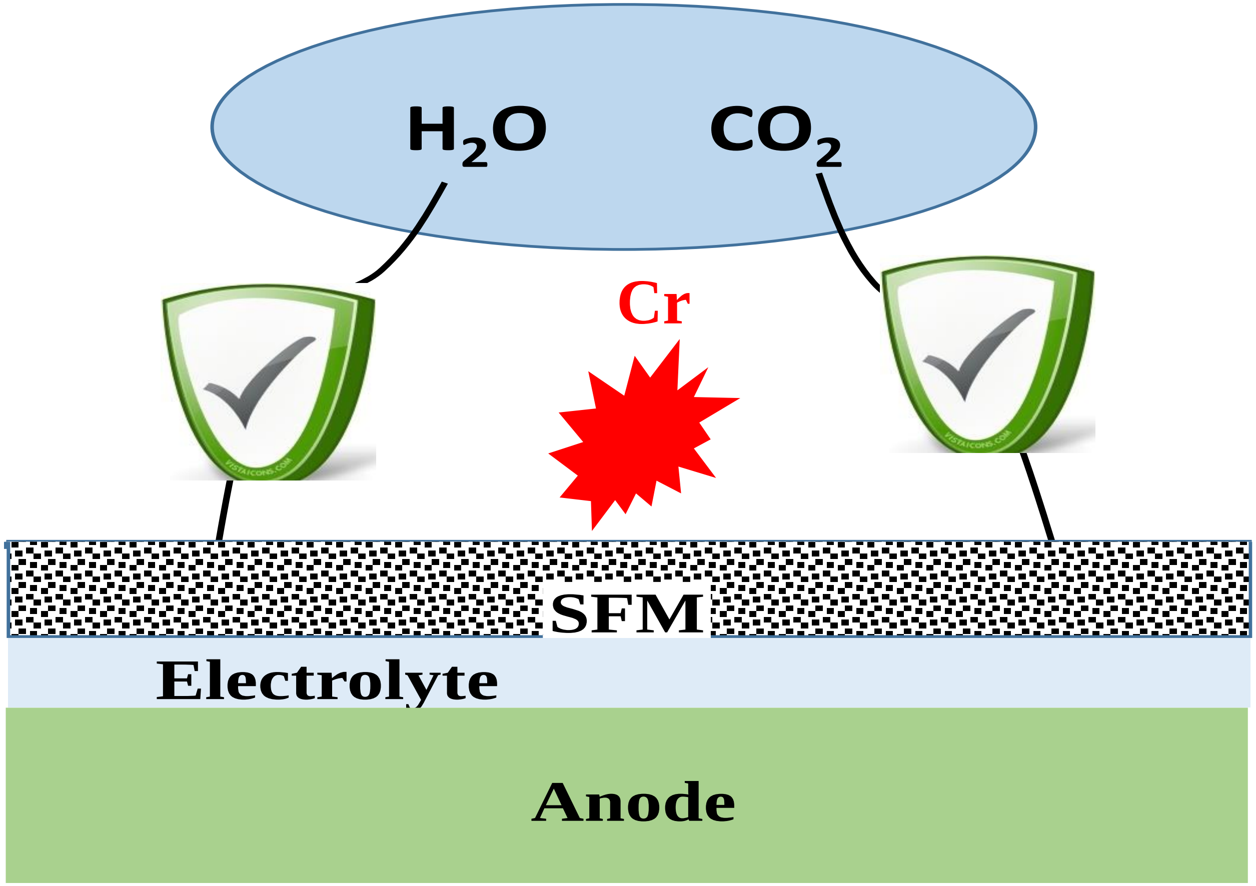


- SFM-GDC electrode before and after short-term test under pristine and Cr-contaminant conditions at 1073K.
- Octahedral-shaped crystals containing Cr are formed

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) Stability w/ Cr-sources



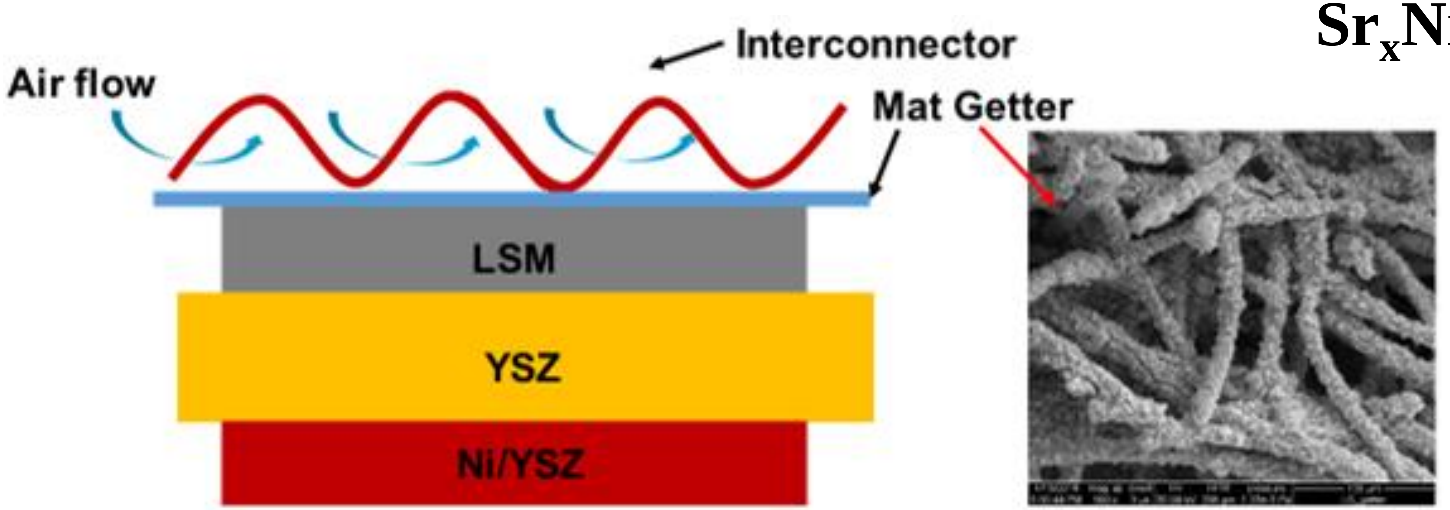
Conclusion 1 – SFM Is Not a Cr-tolerant Cathode



Will SFM Be an Effective Cr-getter?

Cr-Getter

$Sr_xNi_yO_z$



SrO serves as nucleation agent for the formation of $SrCrO_4$

$$CrO_3(g) + Sr_xNi_yO_z \rightarrow SrCrO_4 + NiO + O_2(g) \quad (1)$$

$$CrO_2(OH)_2(g) + Sr_xNi_yO_z + O_2(g) \rightarrow SrCrO_4 + NiO + H_2O\ (g) \quad (2)$$

https://www.netl.doe.gov/project-information?p=FE0027894

Research Objective 2 -- SFM as Alternative Cr-getter?

$Sr_xNi_yO_z$
(Already reported Cr getter)

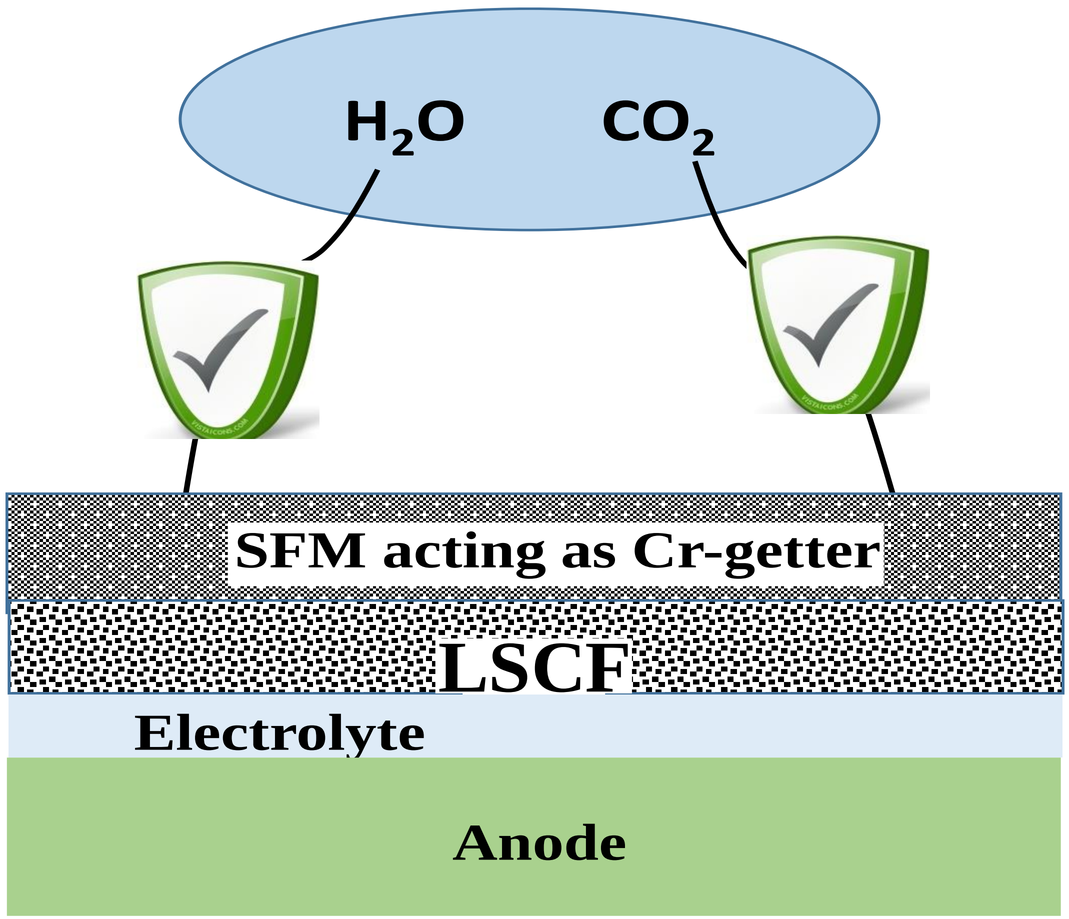
$Sr_2Fe_{1.5}Mo_{0.5}O_6$ (SFM)

$2SrO + Cr_2O_3 + 1.5O_2 = 2SrCrO_4$, $\Delta G = -310\ kJ\ mol^{-1}$ at 1073 K
High Sr content

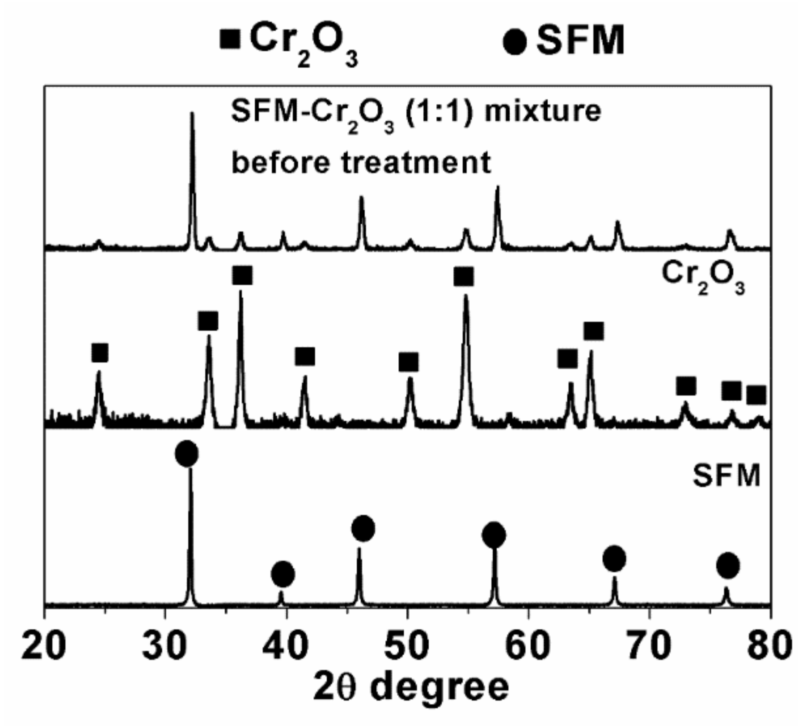
$Sr_xNi_yO_z$	SFM
Instable at above 1223 K	Stable up to 1623 K
Instable in a H_2O-CO_2 containing atmosphere	Stable in a H_2O-CO_2 containing atmosphere
Large volume expansion leads to expansion mismatch with other components of SOFC	Chemically and physically compatible with most cathode materials also with perovskite structure

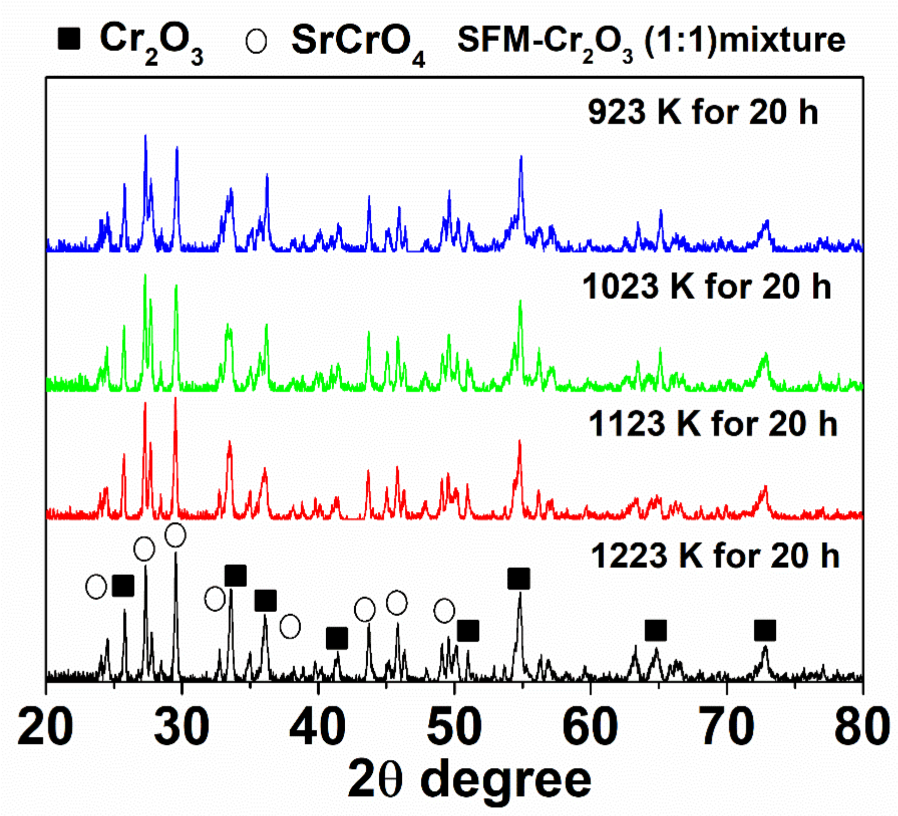
Potential to be a good chromium getter material?

Project Objective 2 – SFM as Cr-getter



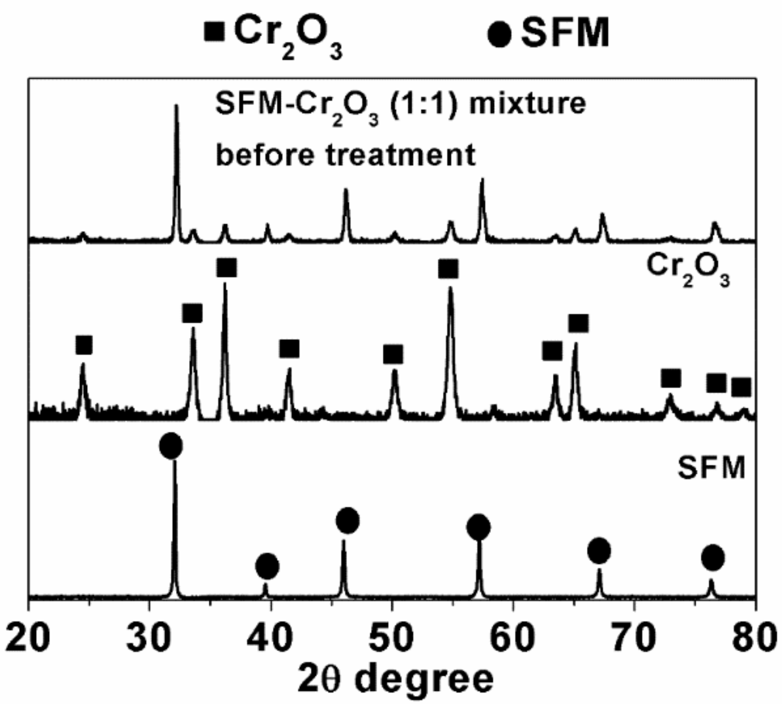
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFM) Reactivity with Cr_2O_3

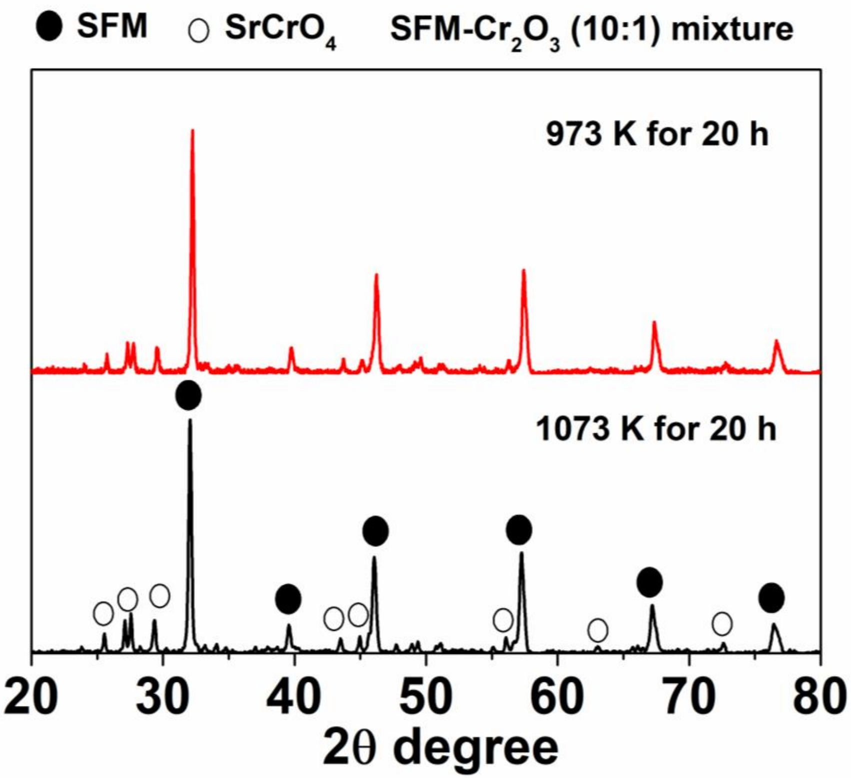




- For SFM:Cr_2O_3 (1:1) mixture with excess Cr_2O_3, SFM phase disappeared and $SrCrO_4$ phase formed.
- Even at 923 K (650^{o}C), SFM still reacts with Cr_2O_3 to form $SrCrO_4$

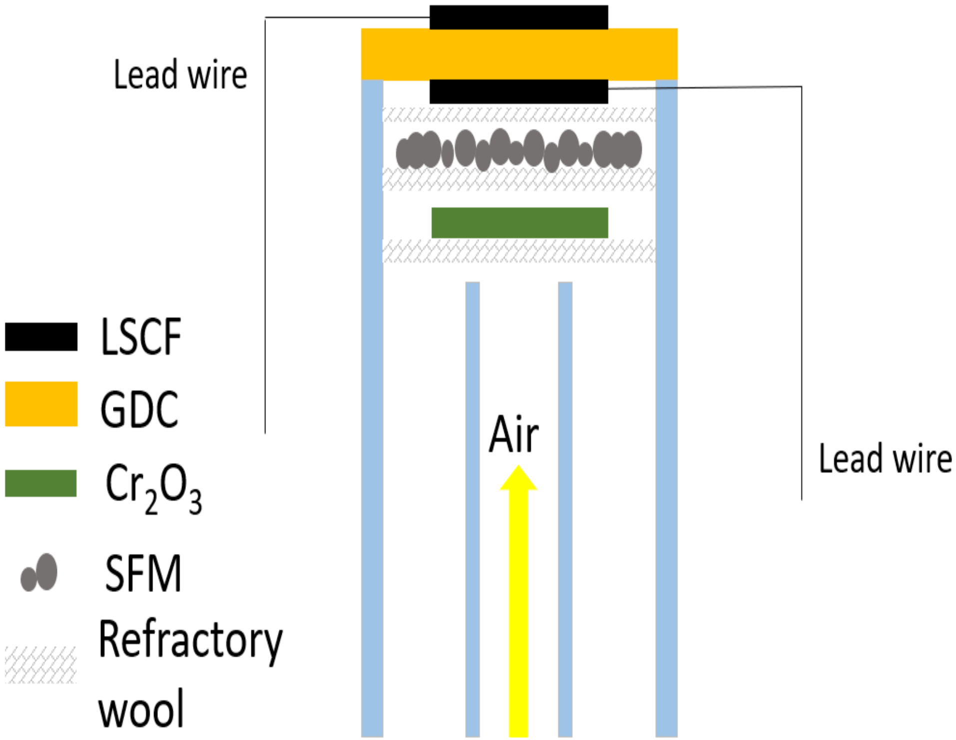
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) Reactivity with Cr_2O_3





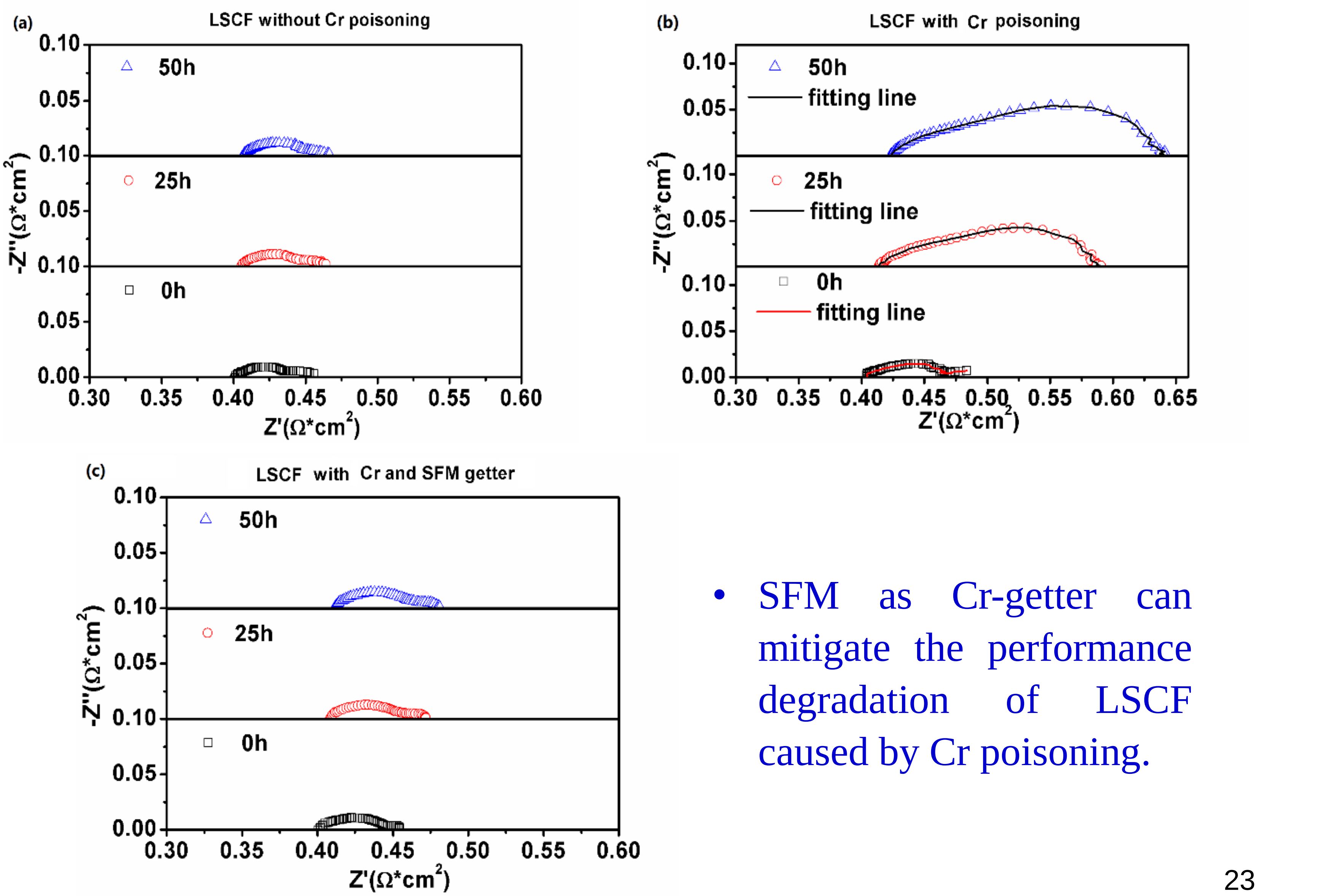
- For SFM:Cr_2O_3 (10:1) mixture with excess SFM, both SFM and $SrCrO_4$ phases can be observed.

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) as Cr Getter for LSCF Cathode



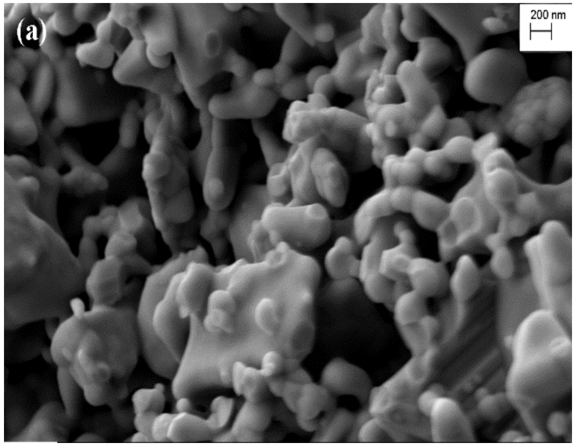
- Symmetrical half-cells of LSCF electrodes on both sides of the GDC electrolyte.
- Porous SFM is placed in the Cr-containing stream.

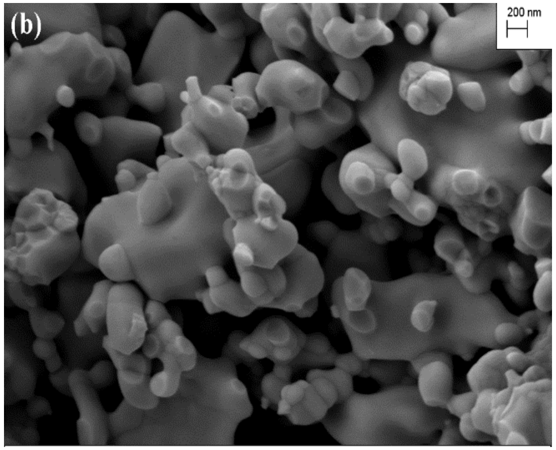
$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) as Cr Getter for LSCF Cathode



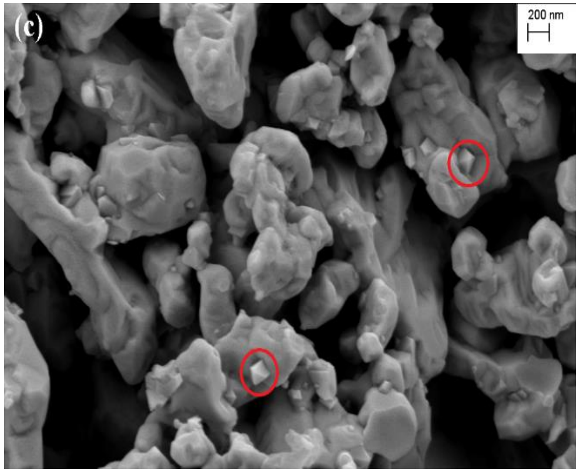
- SFM as Cr-getter can mitigate the performance degradation of LSCF caused by Cr poisoning.

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) as Cr Getter -- LSCF Microstructure

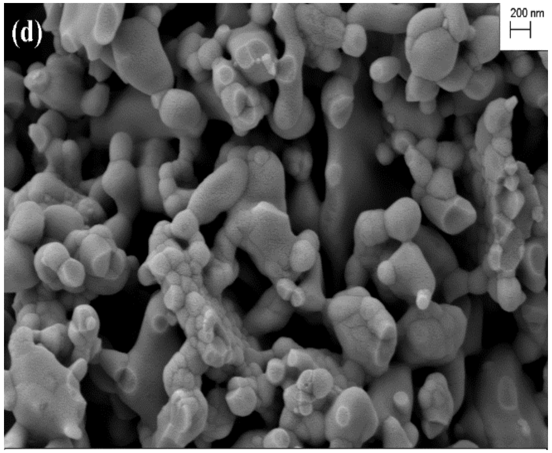




Microstructure characterization of LSCF (a) blank before test; (b) blank after test



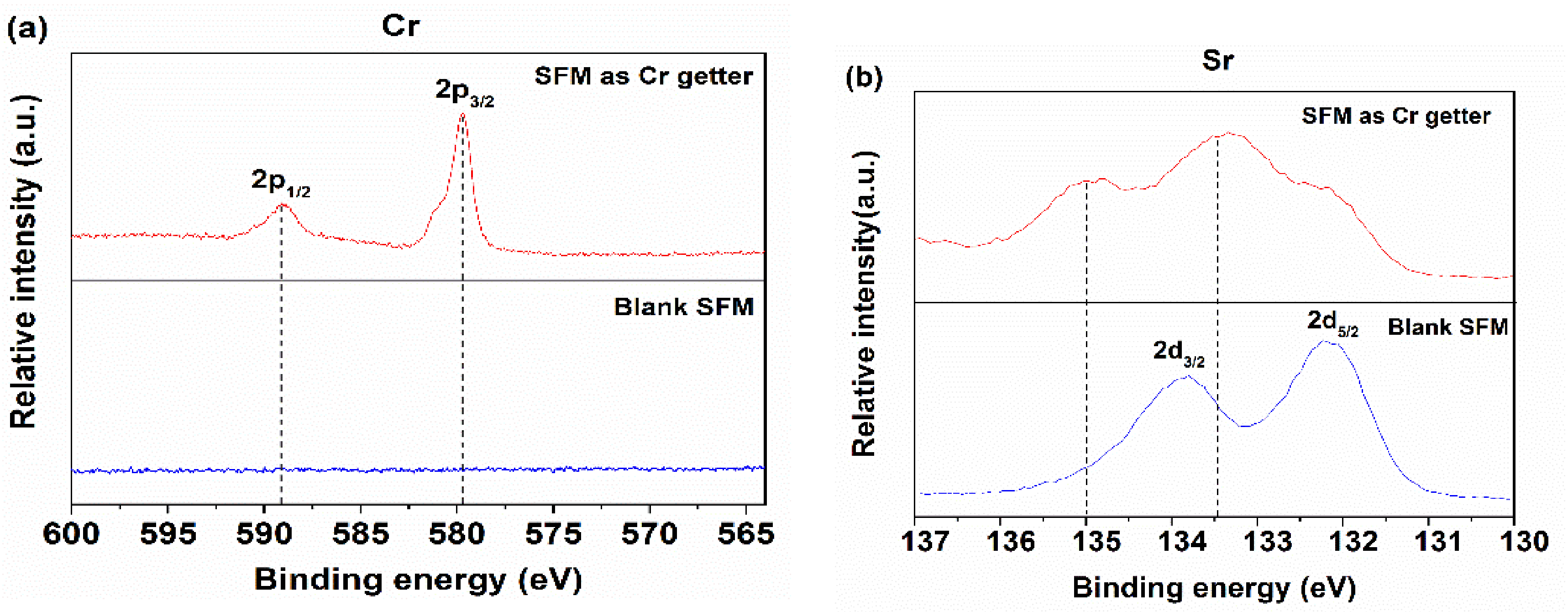
(c) LSCF with Cr source



(d) with Cr source and SFM as Cr-getter

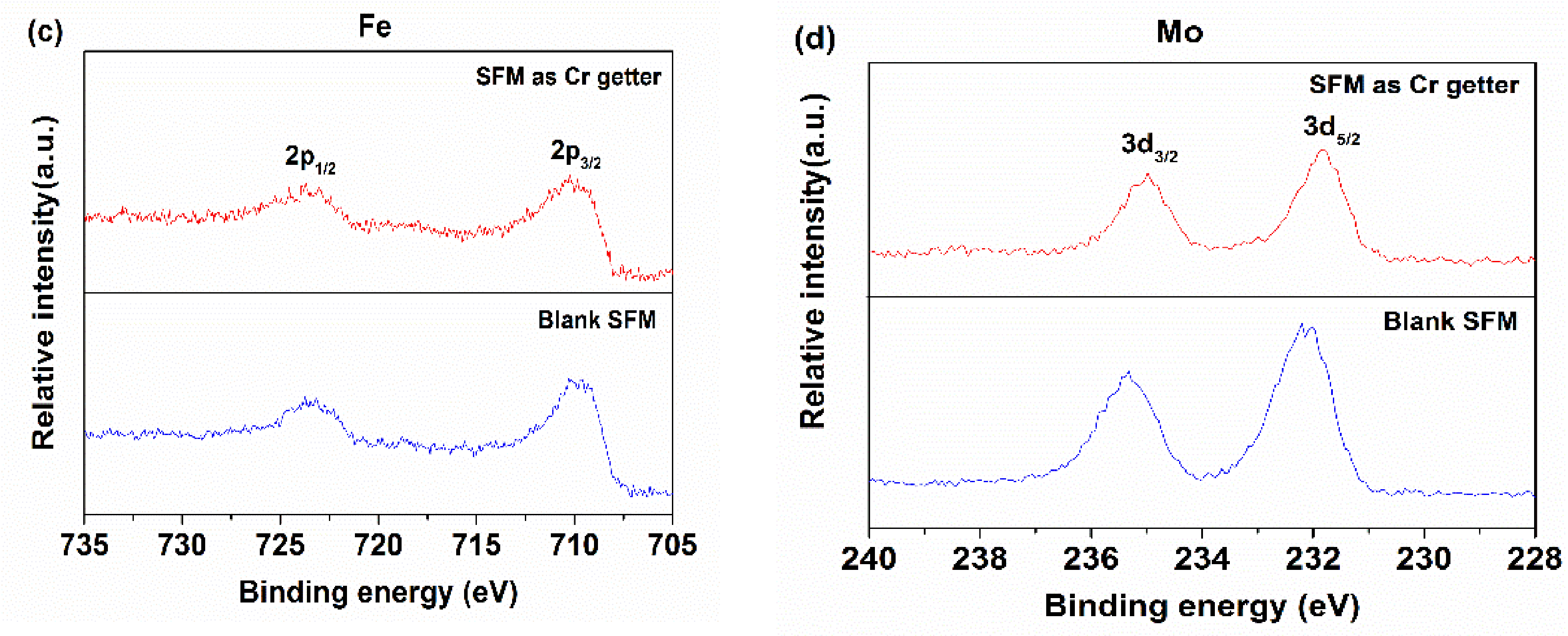
- Octahedral-shaped crystals containing Cr not observable on LSCF with SFM as Cr-getter under Cr-contaminants.

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) as Cr Getter – XPS Study for SFM



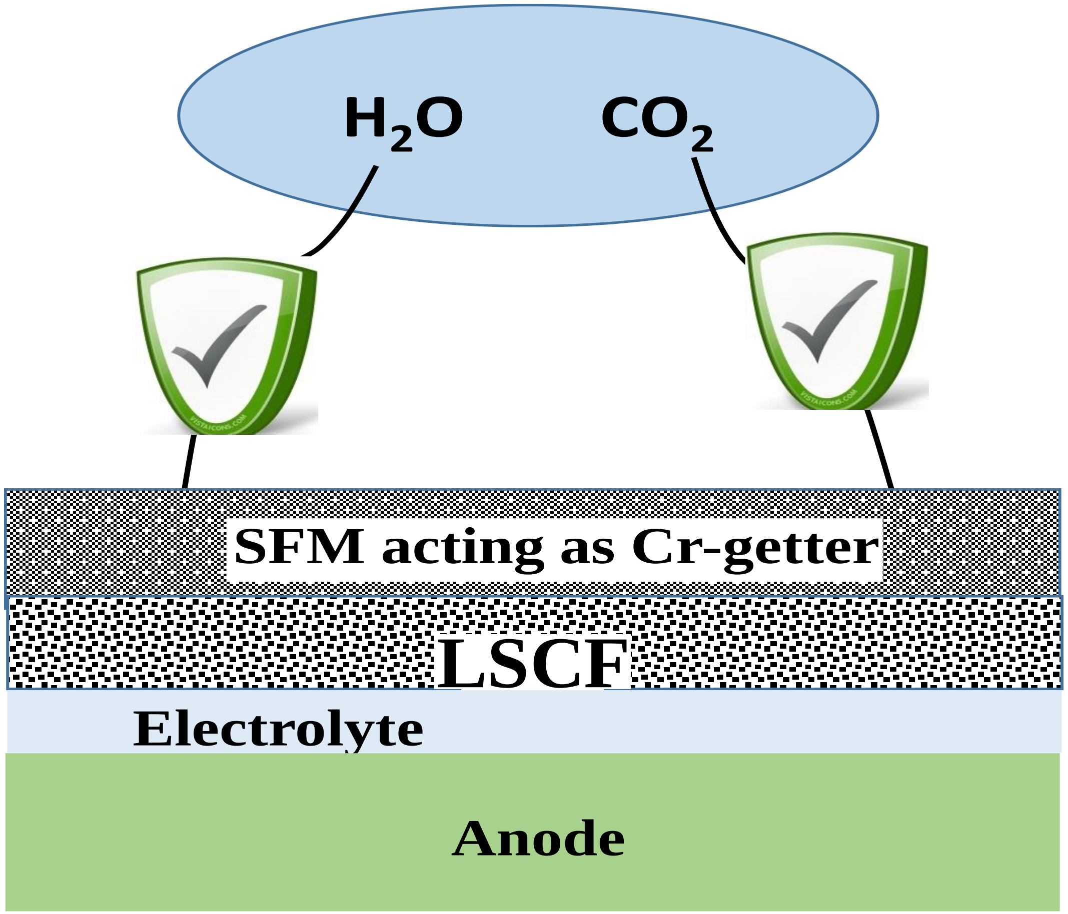
- **No Cr in the blank SFM sample, and peaks corresponding to Cr 2p found in the SFM layer as Cr getter.**
- **The binding energies of Cr 2p $_{3/2}$ and 2p $_{1/2}$ of 580 eV and 589 eV respectively, similar to the typical binding energies of Cr in $SrCrO_4$**
- **Significant changes for Sr XPS spectra. Two new peaks around 133.5 eV and 135 eV can be observed after test. The binding energies of these two new peaks are close to those of Sr in $SrCrO_4$ reported in the literature.**

$Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) as Cr Getter – XPS Study for SFM



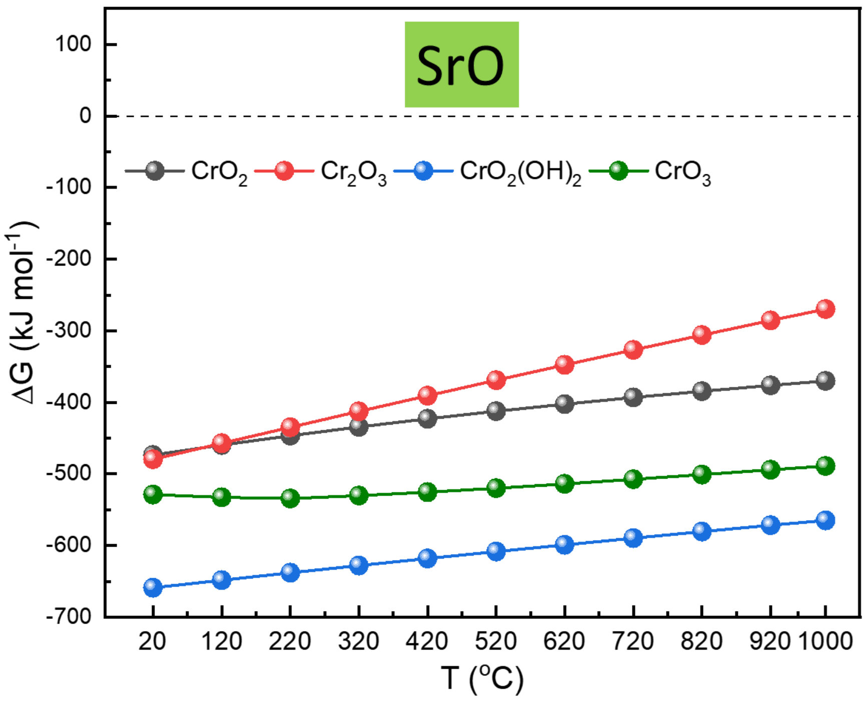
- **XPS spectra of Fe and Mo before and after test are similar, suggesting that Fe and Mo have less reactivity with Cr species than Sr.**

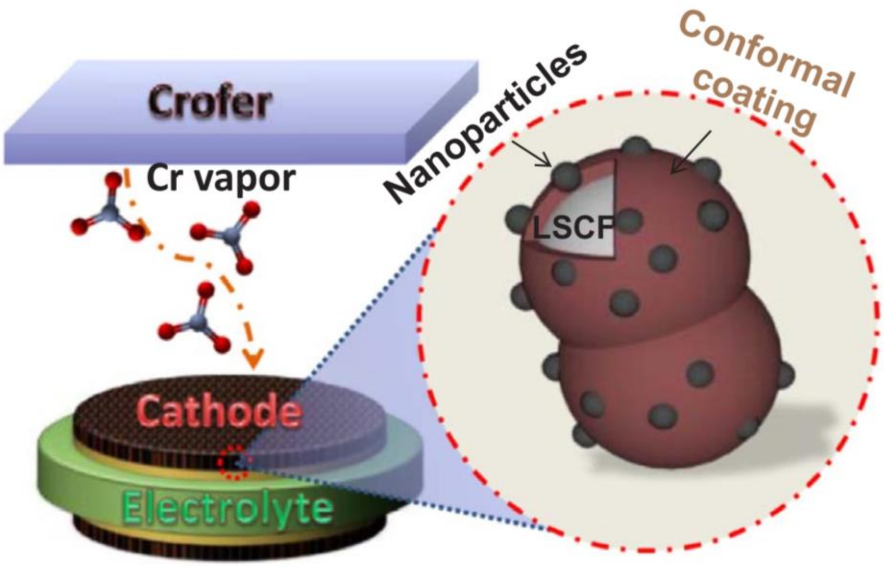
Conclusion 2 – SFM Is an Effective Cr-getter



How to Mitigate Cr-poisoning for Sr-containing Cathode?

How to Mitigate Cr-poisoning for Sr-containing Cathode?

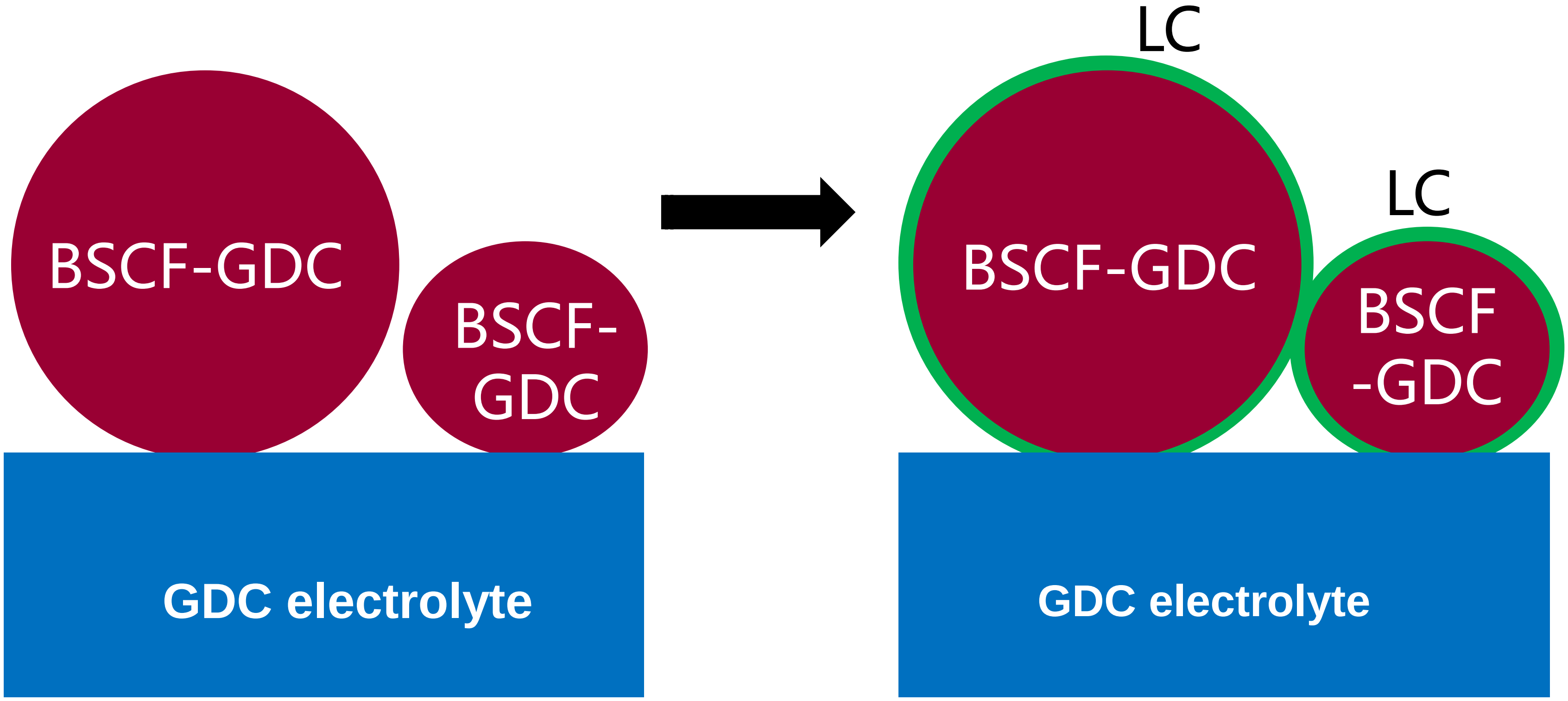




$PrNi_{0.5}Mn_{0.5}O_3$ (PNM) and exsoluted PrO_x nano-particles

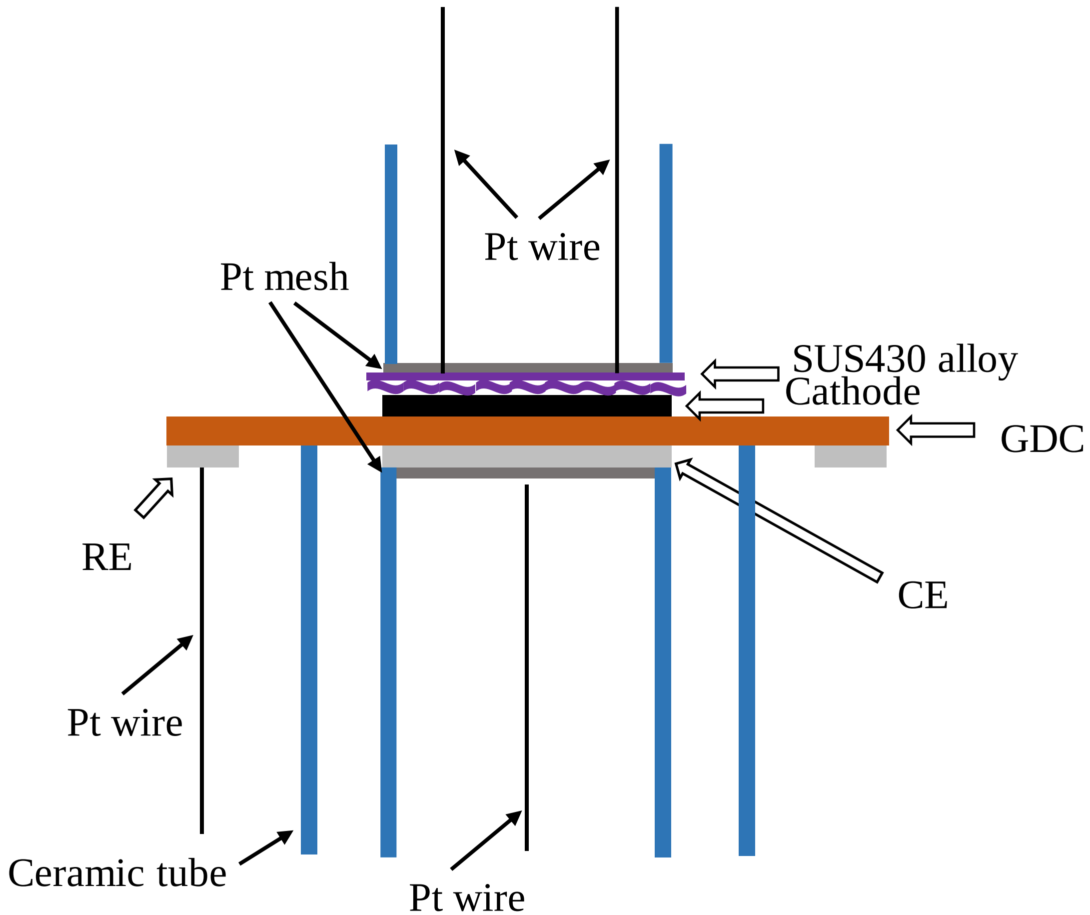
Nano Energy 2018, 47, 474–480

LC-coated BSCF Cathode for Cr-poisoning Mitigation



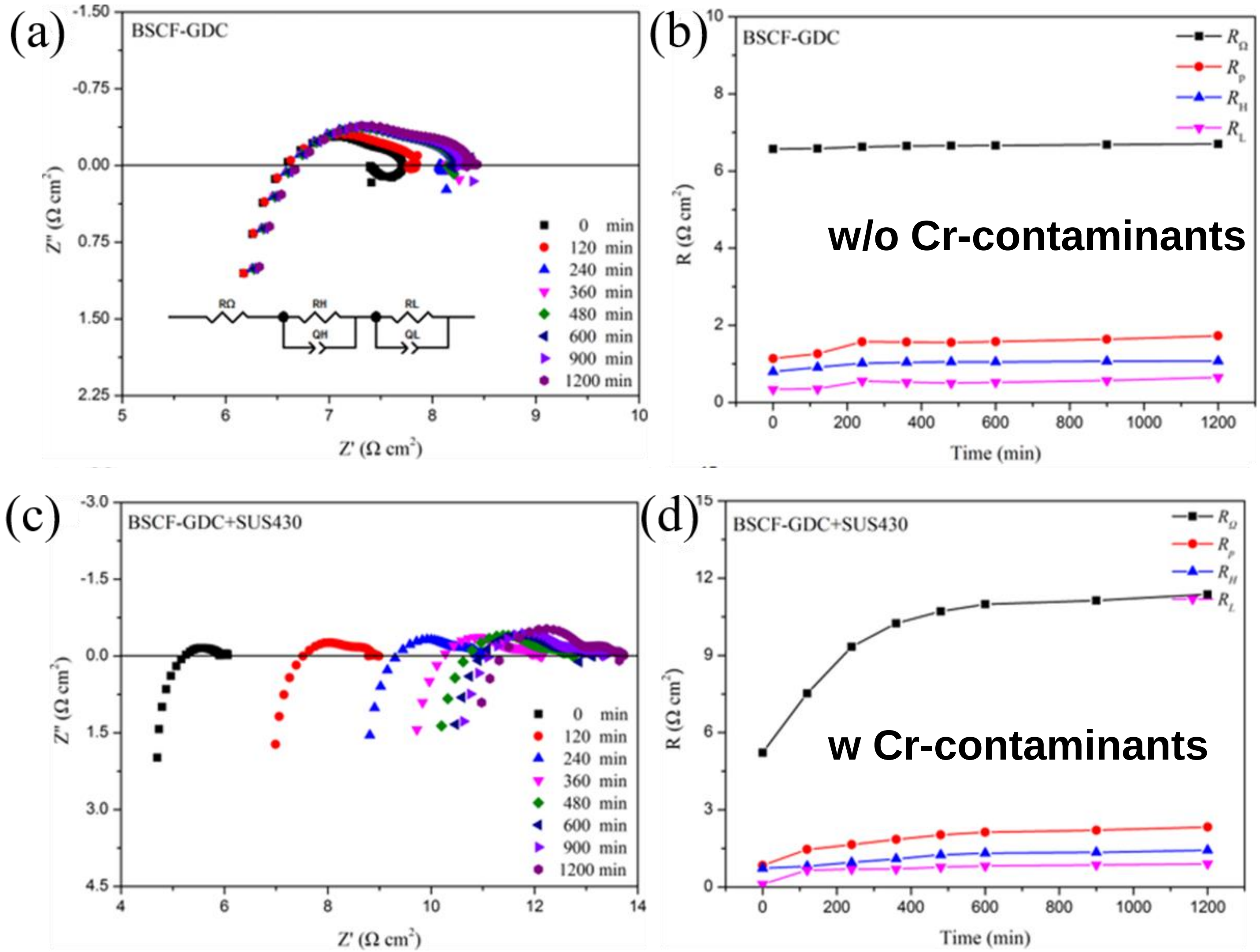
Half cell: BSCF-GDC/GDC/BSCF-GDC

Schematic for Testing Setup for LC-coated BSCF Cathode



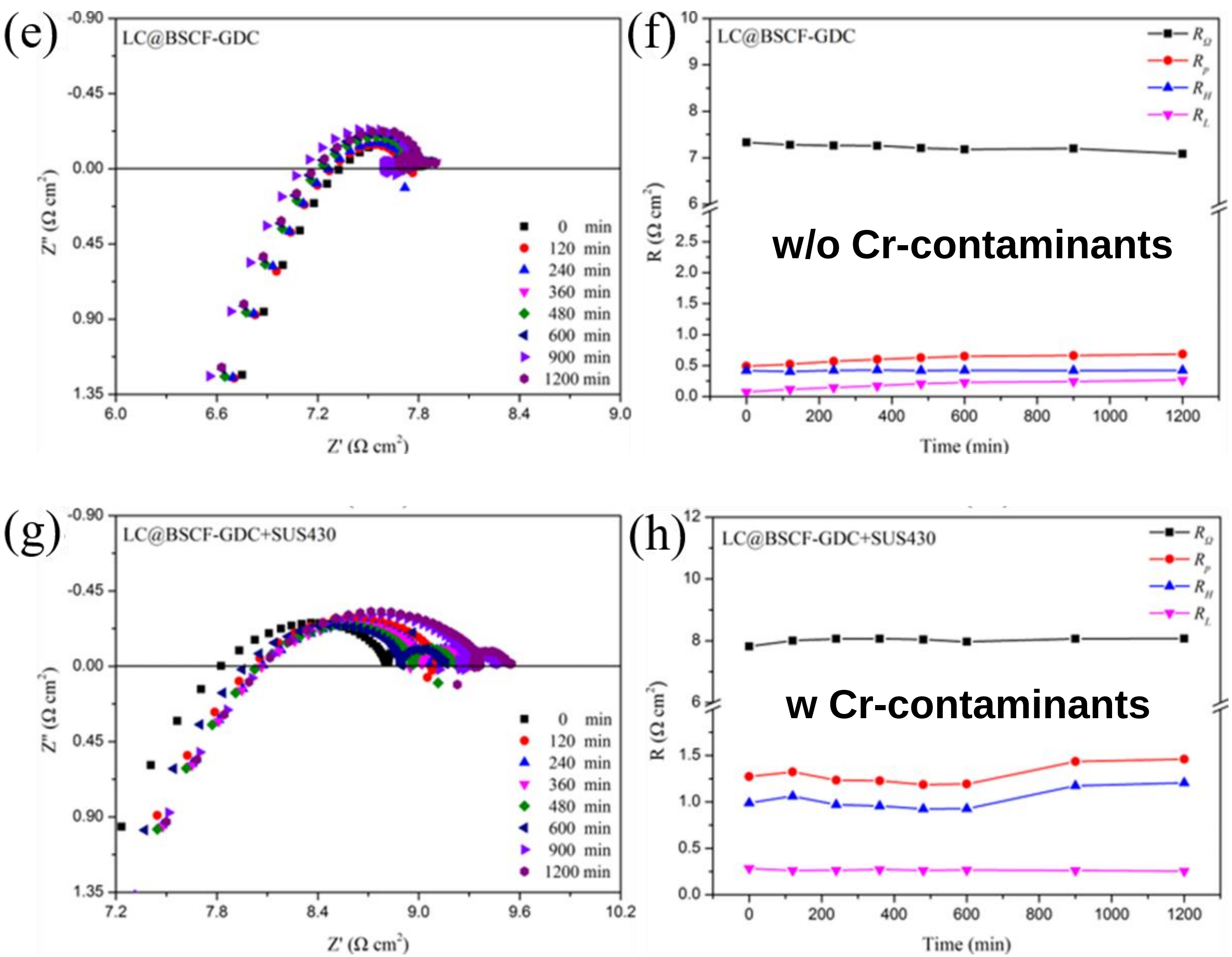
- Symmetrical half-cells of LC@BSCF electrodes on both sides of the GDC electrolyte.

BSCF Cathode w/ and w/o Cr-contamination



- **Ohmic resistance significantly increases under Cr-contamination**

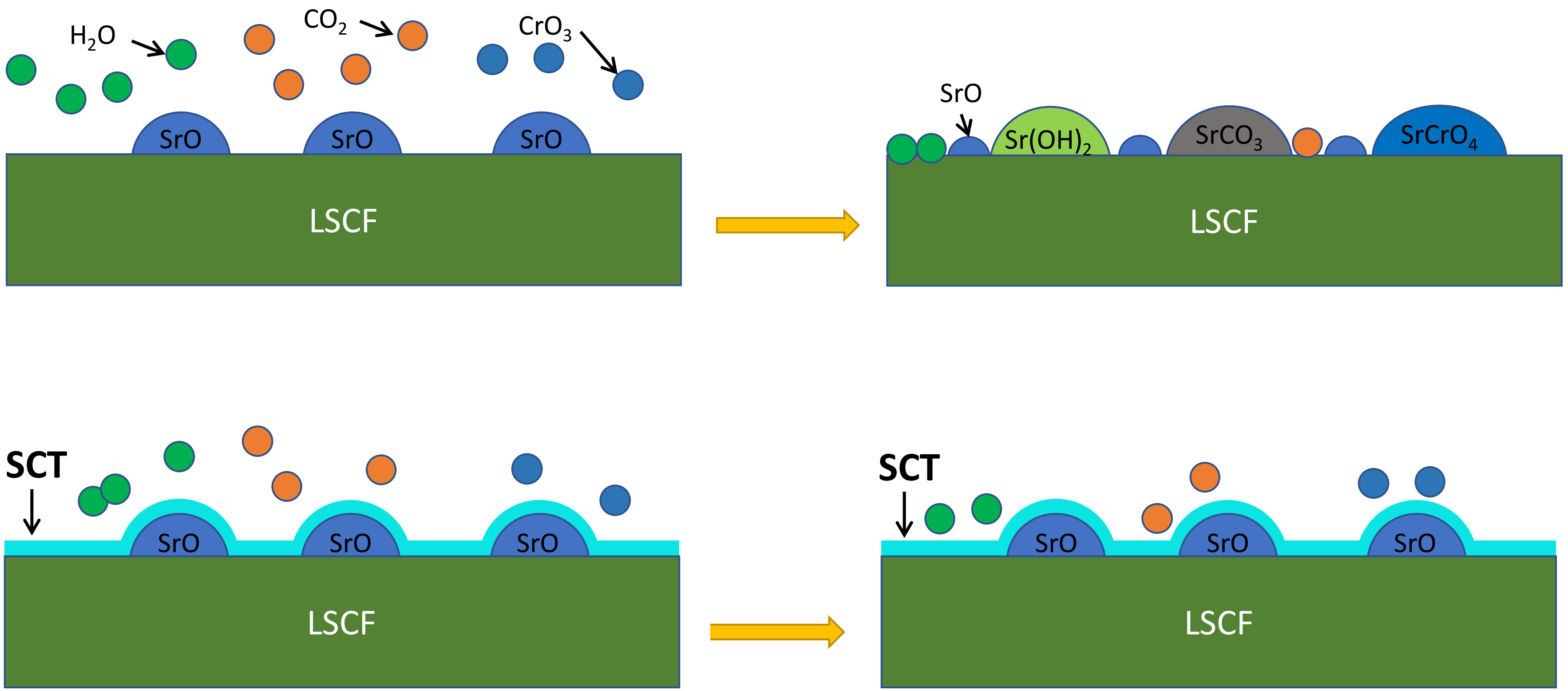
LC-coated BSCF Cathode w/ and w/o Cr-contamination



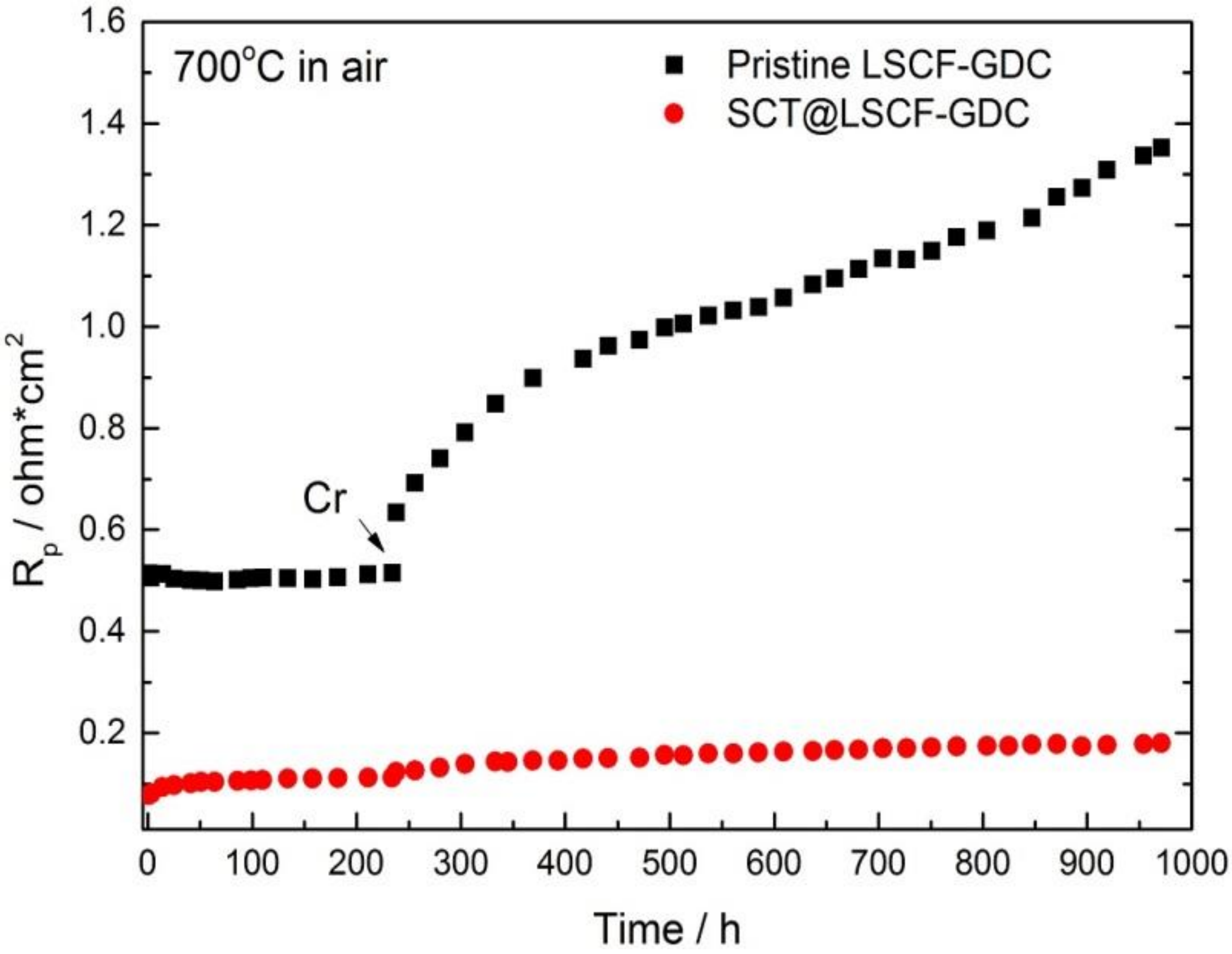
LC-coating significantly enhances performance stability of BSCF

H_2O, CO_2 and Cr Effect on LSCF-GDC and SCT@LSCF-GDC

SCT: Sr-segregation free



New Isostructural Bilayer Cathode Tolerant to Cr



Summary

- $Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) does not possess tolerance to Cr-poisoning.

- $Sr_2Fe_{1.5}Mo_{0.5}O_{6-d}$ (SFM) is an effective Cr-getter.

- Coating the appropriate compositions can significantly enhance performance stability of Sr-containing cathode

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